

# MEMORY SWITCHING AND OPTICAL PROPERTIES OF GLASS-METAL MICROCOMPOSITES

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to the

INTERDISCIPLINARY PROGRAMME IN MATERIALS SCIENCE  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
JANUARY, 1982

Dedicated

to my

Parents



## CERTIFICATE.- I

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MS 607 Amorphous Solids

MS 620 Materials Engineering

Met 668 Structure and Properties of Glass

MS 602 Materials Science II

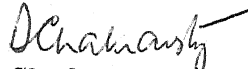
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## SYNOPSIS

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Glass-metal microcomposites consist of a glass phase containing a distribution of metallic particles having dimensions of the order of a few hundred angstroms. These materials are extensively used in photosensitive glasses, photosensitively nucleated glass-ceramics, photochromic glasses, photothermal conversion, solar coatings etc. Recently memory switching properties have been found in certain oxide glasses containing bismuth particles of a few hundred angstroms dimension. In this thesis a detailed theoretical model has been developed to explain the various features of this switching. Also the optical absorption characteristics of these materials have been delineated over a range of frequency spectrum and the results are explained on the basis of various theoretical models.

Chapter 1 gives a brief literature survey on research in glass-metal microcomposites.

Chapter 2 deals with the theoretical model. According to this, a two-stage process sets in when an electric field is applied to the specimen. Firstly, Joule heating raises the sample temperature sufficiently to cause the metallic granules to melt. Subsequently, the electric field stretches the molten granules against the surface tension force and at the threshold field, the granules touch each other thereby causing the material to switch to the "on" state. A one dimensional heat equation has been solved numerically to find the electrical field necessary to raise the temperature to the effective melting point of bismuth particles. However, the critical field necessary to stretch the molten granules so that they touch each other is found to be larger than the previous one and hence determines the overall switching field. The values of the latter for different particle diameters and separation to diameter ratios have been calculated. These compare reasonably well with experimental data obtained in the cases of silicate and vanadium phosphate glasses containing bismuth particles.

In Chapter 3, the voltage-current characteristics of vanadium phosphate glasses containing bismuth granules especially in the negative resistance region have been computed using the model developed in Chapter 2. It is shown that according to the mechanism proposed first a conducting region is formed at the specimen centre due to the metal spheres touching each other. A regenerative process then sets in as a result of increase in the current flow through the specimen ultimately leading to the "on"

state when the percolation of the metal phase in the glass matrix is attained. One dimensional time dependent heat equation has been solved numerically at different instants of time to delineate the corresponding temperature profile within the sample and the concomitant changes in its resistance and the current flow through it. Experimental measurements on well-characterized specimens in the  $V_2O_5-P_2O_5-Bi_2O_3$  system have been carried out and the results are compared with the theoretical values. Satisfactory agreement between the two has been obtained. It is observed that increase in sample thickness leads to a threshold switching. For a memory switched sample measurement of its resistance in the "on" state as a function of temperature shows that in the range  $75^\circ C - 110^\circ C$  it reverts back to the off state through a voltage controlled negative resistance in the range 0.2 to 0.5 volt. All these have been explained on the basis of the present theory.

In Chapter 4, the kinetics of switching has been investigated by solving numerically fluid flow equations corresponding to the movement of boundaries of the molten granules during the stretching process. Switching time has been measured experimentally by applying electrical pulses on samples in  $V_2O_5-P_2O_5-Bi_2O_3$  system at room temperature and monitoring changes in their resistance. Experimental values (in the range 50 - 80 microseconds) are found to be orders of magnitude higher than the theoretical prediction ( $\sim 10^{-9}$  second). However, the

switching time computed from the solution of time dependent heat equation is in reasonable agreement with experimental data. It is concluded, therefore, that the kinetics is controlled primarily by the Joule heating step.

In Chapter 5, the optical properties of vanadium phosphate as well as sodium borosilicate glasses containing bismuth granules of dimensions of the order of a few hundred angstroms have been investigated. The microstructures of samples having different compositions and subjected to various reduction treatments have been characterized by transmission electron microscopy. Optical absorption in the visible range has been measured using Carry 17D Spectrophotometer. Vanadium phosphate glasses containing bismuth show an absorption peak around  $(450 \pm 10 \text{ nm})$  while the silicate glasses containing bismuth show two peaks in the ranges 500 nm - 530 nm and 420 nm - 430 nm respectively. The peak position in  $V_2O_5-P_2O_5-Bi_2O_3$  glasses is predicted in fair agreement with experiment by Maxwell-Garnett (MG), Maxwell-Garnett as extended by Polder and Van Santen (MG-PVS) and Bruggeman (BR) effective medium theories with MG theory giving the best fit. In the case of silicate glasses containing bismuth the predicted positions do not agree so well with experimental results. The possibility of a fraction of the metal spheres being present in the form of interconnected metallic chains and/or f.c.c. clusters in the present microcomposites has also been explored. A typical computation has been carried out by using a constrained optimisation technique with some

assumed fractions of spheres, f.c.c. clusters and single strand chains as the optimising parameters. It is observed that in a vanadium phosphate glass containing bismuth quantitative agreement between the computed and experimental  $\alpha$  values within an error of 4% over the entire spectral range can be achieved if the metallic phase is assumed to consist of 26% spheres 0.6% single strand chain and 73.6% f.c.c. clusters.

In Chapter 6, the main conclusions drawn on the basis of the entire investigation are summarised.

## CHAPTER 1

### INTRODUCTION

#### 1.1 Applications of Glass-Metal Microcomposites

Glass-metal microcomposites consist of a glass matrix with a distribution of metallic particles in the range of a few hundred angstroms in size. The metallic particles may be precipitated either during melting, controlled cooling of the melt or during subsequent heat treatment depending on the glass compositions and melting conditions. The applications of glass-metal microcomposites may be broadly classified as follows<sup>1</sup>.

1. Photosensitive glasses
2. Photosensitively nucleated glass-ceramics
3. Photochromic glasses
4. Polychromatic glasses
5. Photothermal conversion (cermet)
6. Solar control coatings (electro float process)

Some of the other possible applications will be :

1. Electro-conducting glasses and fibres
2. Memory switching
3. High strength glasses and fibres

A brief review of the present state of research of the glass-metal microcomposites is presented in the following sections.

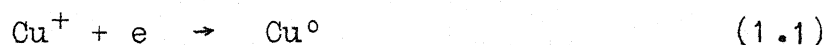
## 1.2 Photosensitive Glasses

In photosensitive glasses, metallic granules of colloidal dimensions are precipitated by subjecting the glass to certain heattreatment schedules. The precipitation is greatly enhanced if the glasses are exposed to UV radiation prior to heat-treatment<sup>2</sup>.

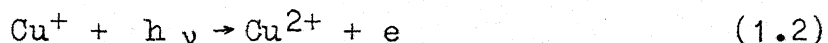
Weyl<sup>3</sup> considers that copper, silver and gold may be present in glass in true solution and they get precipitated either by controlled cooling of the molten glass or by subsequent heating of the same. The relative proportions of ions ( $\text{Cu}^+$ ,  $\text{Ag}^+$  and  $\text{Au}^{3+}$ ) and the corresponding metallic atoms depend on the melting condition and the composition of the glass. When the molten glass is quickly cooled the high temperature state is retained and the glass remains colourless. The glass strikes the colour when it is subjected to a heat-treatment. The mechanisms involved are as follows. During heattreatment the reducing agents, e.g.,  $\text{SnO}$ ,  $\text{As}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$  etc. get oxidised after reducing suitable ions in the melt to their metallic counterparts. These metal atoms along with those which are already present in the matrix nucleate and grow to colloidal dimensions. These metallic granules are responsible for the selective absorption of light and so colour is developed. In this connection, it should be mentioned that platinum in the form of colloidal dispersion has not been used as colourant, because this leads to greyish tint. However, the importance of

colloidal platinum is that it can be used as a nucleation catalyst to prepare glass-ceramics. In contrast to copper, silver and gold no heattreatment is necessary to form colloidal platinum<sup>4</sup>. The platinic chloride which is usually added as the source of platinum breaks during melting to form platinum colloids in the melt.

The earliest photosensitive glasses contain copper as the photosensitive element. In later development it has been shown that silver and gold can also act as photosensitive elements. A range of photosensitive glass compositions containing these elements have been worked out by Stookey<sup>5</sup>. The fundamental mechanism of the photosensitive process involves two steps. The glass is first irradiated selectively by placing a photographic negative to form the latent image. This is achieved by reducing the ions to their atomic states as follows :



The electron necessary for this reduction reaction is obtained by photo-assisted oxidation of  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  ions, according to the following reaction,

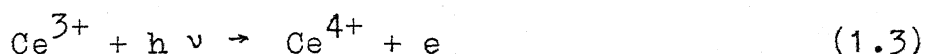


The irradiated glass is then subjected to a heattreatment in the temperature range of 500°C-600°C for a suitable period of time. Since the irradiated portion of glass contains more metallic atoms the metallic phase nucleates and grows to give



colour and thus the latent image is developed.

It has been shown by Stookey<sup>6</sup> that inclusion of cerium oxide in the glass batch greatly improves the photosensitivity. This is essentially due to the ease with which electrons are made available by the reaction,



Gold and silver are introduced in the photosensitive glass batches as their chlorides. The glass batches are melted in oxidising condition. The amount of silver present is equivalent to 0.05% of 0.3% AgCl, while the concentration of gold varies in the range of 0.01% to 0.1%. On the other hand glasses containing 0.05 to 1.0% of copper (calculated as  $\text{Cu}_2\text{O}$ ) as photosensitive element are melted in reducing atmosphere. The glasses contain small amount of  $\text{Sb}_2\text{O}_3$  (about 0.1%) along with cerium oxide. The beneficial effects of  $\text{Sb}_2\text{O}_3$  lie in the fact that it provides electrons by being oxidised to  $\text{Sb}^{5+}$  ionic state.

### 1.3 Photosensitively Nucleated Glass-ceramics

The process of photosensitively nucleated glass -ceramics involves three steps. Firstly, the chilled glass is exposed to UV radiation so that the formation of metal atoms takes place. Secondly, the glass is heattreated to a temperature which depends on the system used, for a certain period of time so that sub-microscopic metallic particles get precipitated by a process of

nucleation and growth. Lastly, the glass is further heated to higher temperatures when the metallic granules act as heterogeneous sites for controlled crystallisation of glass. This is one of the early methods of producing glass-ceramics.

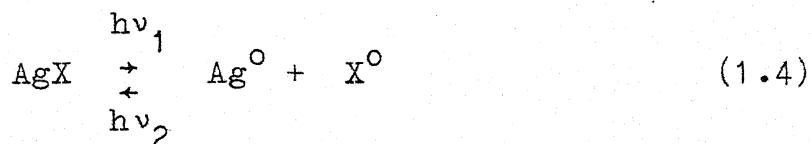
Stookey<sup>7</sup> has studied many glasses of the  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system. These glasses contain either gold in the range of 0.001% to 0.003% or copper in the range of 0.001% to 1.0% (computed as  $\text{Cu}_2\text{O}$ ) or 0.001% to 0.3% of silver (calculated as  $\text{AgCl}$ ). The glasses are exposed to UV radiation followed by heat treatment at  $500^\circ\text{C}$ - $540^\circ\text{C}$  and subsequently heat treated at temperatures around  $950^\circ\text{C}$  to produce the glass-ceramics. These materials have good mechanical strength and electrical properties. In a later development it has been shown by Stookey et al.<sup>8</sup> that there is a minimum size of metal namely  $80 \text{ \AA}$  below which they cannot act as nucleation catalysts to crystallise lithium metasilicate. Rindone<sup>4</sup> has studied the use of metallic platinum as heterogeneous nucleation catalyst to crystallise lithium silicate glasses. It has been demonstrated that an optimum amount of platinum (0.004% to 0.007% at  $600^\circ\text{C}$ ) is needed to get maximum crystallisation. It has been shown that there is an optimum radiation dose necessary for the photosensitively nucleated gold containing lithium aluminosilicate glass-ceramics to attain the maximum mechanical strength<sup>2</sup>.

#### 1.4 Photochromic Glasses

When photochromic glasses are exposed to sunlight they

darken and fade when the light is removed. This is a reversible process. A similar process called solarisation has been known for many years. In contrast to photochromic glasses the latter are sensitive to high energy electromagnetic radiation. Recently, Araujo<sup>9</sup> has reviewed different aspects of photochromic glasses.

Armistead et al.<sup>10</sup> have developed alkali aluminoborosilicate system which has perhaps been . . . most thoroughly studied. The other systems investigated are alkali and alkali earth borates<sup>11</sup>, heavy metal aluminoborates<sup>12</sup> to name a few. The silver halide crystal which gets precipitated, induces photochromic properties. The mechanism involved is believed to be quite analogous to that operative in photographic films. When the photochromic glass is irradiated with light silver halide is decomposed into silver and halogen. Unlike the photographic film, the liberated halogen is trapped into close proximity of silver due to the rigidity and impermeability of glass. When light is removed the silver and the halogen atoms recombine and revert to transparent colourless silver halide crystals. The reversible reaction, which causes darkening and fading of photochromic glasses can be represented as follows<sup>13</sup> :

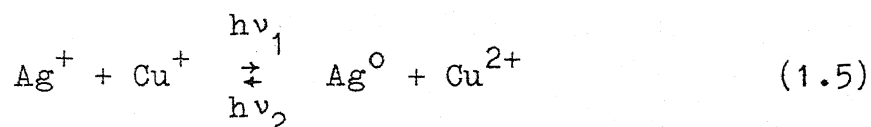


In many photochromic glasses, the absorption band is found near 500 nm and this is attributed to colloidal silver by Moriya<sup>14</sup>.

Seward<sup>15</sup> suggests that ellipsoidal silver particles are responsible for optical absorption in the visible range. The theoretical model explaining the behaviour of photochromic glasses can be found in a review article by Araujo<sup>9</sup>.

If the glass is cooled very rapidly from molten state, photochromic property is not developed because no silver halide particles are precipitated. To develop photochromism a subsequent heat treatment is necessary. There is an optimum range of silver halide particle size, namely 80-150 Å. If the particles are smaller than the lower limit the glasses do not darken at all. On the other hand if the particles are larger than the upper limit the glasses become hazy. Since the increase of subsequent heat treatment temperature increases the particle size usually silver halide containing photochromic glasses are heat treated in the temperature range of 400°-800°C for 15 minutes to 4 hours<sup>9</sup>. After the precipitation of silver halide particles, further low temperature heat treatments have profound influence on photochromic properties<sup>16,17</sup>. The combined influence of compositions and different heat treatment temperature for different periods of time of some glasses in the alkali aluminoborosilicate system has been studied by Hares et al.<sup>18</sup>. It indicates the importance of base glass compositions and thermal history on the darkening and fading characteristics of the photochromic glasses. Gliemeroth<sup>19</sup> has discussed the

properties of photochromic glasses as a function of temperature and radiation dose. This is important from the point of view of applications in different weather conditions. The presence of copper in small amount ( ~ 0.02%) increases the darkening sensitivity very effectively<sup>13</sup> as it augments the production of neutral silver atoms according to the reaction,



Similarly the presence of cadmium only in presence of copper<sup>20</sup> enhances the darkening sensitivity. Along with the composition as mentioned earlier, the melting conditions can affect the photochromic properties as they strongly influence the retention of halide and oxidation states of copper and silver in the glass melt.

We have, so far, discussed the photochromic glasses containing the silver halide particles. However, highly reduced homogeneous alkali silicate glasses<sup>21</sup>, CdO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses<sup>22</sup>, Na<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>.1/2NaX<sup>23</sup> (X being chloride or sulfide) glasses show photochromic behaviour also. Glasses containing suspension of crystallites-hackmanite, silver molybdate<sup>24</sup>, thallium chloride<sup>25</sup> and copper cadmium halides<sup>20</sup> show photochromism.

The thermally darkenable photochromic glass (TDPC) is quite different from the usual photochromic glasses. Unlike the latter the TDPC glasses are dark at room temperature and become darker with further heating. When exposed to visible

light the glasses bleach to colourless state at a rate dependent on the intensity of light. On removing the source of light the TDPC glasses returns to darkened state at a temperature dependent rate. Seward III<sup>26</sup> has described the TDPC properties of lanthanum borate based glasses containing copper doped silver halide crystals. The composition ranges of these lanthanum borate glasses can be found in the patent literature<sup>27</sup>.

Seward III<sup>26</sup> has observed high temperature bistable optical states of TDPC glasses. When the glasses are heated in the temperature range of 400°-450°C, they are bleached to a colourless state. When the temperature is lowered to the range of 300°-350°C, they spontaneously go to a darkened state and do not bleach despite the presence of intense light. These two bistable states are believed to arise due to melting and precipitation of silver halide crystals<sup>28</sup>.

The proposed mechanism of TDPC glasses is the precipitation of colloidal silver from the molten silver halide droplet of nonstoichiometric composition during the crystallisation of the latter. Copper may act as either  $\text{Cu}^+$  hole trap or  $\text{Cu}^{2+}$  electron trap and may take part in the optical bleaching or the thermal darkening. On the other hand its only role may be the controlling of oxidation states and hence producing more neutral silver atoms required for the precipitation of colloidal silver from molten halide droplets.

## 1.5 Polychromatic Glasses

The polychromatic glasses are a special kind of photo-sensitive glasses. A variety of colours can be generated by the application of controlled thermo-optical treatments.

The sequence of steps involved to form the polychromatic glass is as follows<sup>29</sup>. Firstly, the glass is exposed to UV radiation to precipitate the small silver particles and this is assisted by the presence of  $\text{Ce}^{3+}$  photosensitisers. In the second step the glass is subjected to a heattreatment such that the silver particles act as heterogeneous sites for the nucleation and growth of sodium halide microcrystals. It has been shown by Stookey<sup>30</sup> that the sodium halide crystals have cubic base with different degrees of pyramidal protrusion. A second UV exposure followed by heattreatment serves to produce silver at the tips of the sodium halide crystals. The amount of silver is related to the type of colour generation<sup>30,31</sup>.

The colour which is obtained is primarily a function of the first UV exposure. A strong UV exposure produces a large number of silver particles and hence a large number of sodium halide crystals is precipitated as a result. The second UV exposure produces a relatively fixed amount of silver. This amount of silver is then distributed over the tips of the crystals. So, if the number of sodium halide crystals is less it produces longer and larger specks (higher aspect ratio) compared to the case when the number of crystals is large. This aspect ratio

controls the generation of colour in polychromatic glasses.

## 1.6 Photothermal Conversion

The efficiency of photothermal conversion of selective black absorbers can be increased by increasing the absorptivity over the solar radiation spectrum and by decreasing the infrared emissivity. In principle this can be obtained in a single material. However most of the selective black absorbers now available is produced by depositing a thin film of metal-dielectric composite which is transparent in the infrared range but highly absorbing in the visible range, on a metal substrate which has low infrared emissivity. The commonly used photothermal conversion materials are electroplated Ni-black, Cu-black on metal sheets. The operating temperature required for photothermal conversion may vary from  $400^{\circ}\text{C}$  -  $1000^{\circ}\text{C}$ . However, the Ni-black and Cu-black are not stable above  $200^{\circ}\text{C}$  while Cr-black is not much stable above  $200^{\circ}\text{C}$ . The  $\text{MgO}/\text{Au}^{32}$  cermet film has been produced by rf sputtering on metallic sheet. It has excellent solar absorptivity viz., over 0.9 and its infrared emissivity is less than 0.1. With Mo metal sheet the selective black absorber is stable upto  $400^{\circ}\text{C}$ . The  $\text{Cr}_2\text{O}_3/\text{Cr}^{33}$  rf sputtered film on metal has solar absorptivity and infrared emissivity similar to  $\text{MgO}/\text{Au}$  cermet film. Its behaviour remains essentially unchanged even after heating at  $300^{\circ}\text{C}$  for 60 hours. The co-sputtered  $\text{Ni}/\text{Al}_2\text{O}_3^{34}$  cermet film on metal has also similar absorptivity and emissivity but it is thermally more



stable (stable upto  $500^{\circ}\text{C}$ ) as compared to other films. Recently, Niklasson et al.<sup>35</sup> have shown by detailed optical study on evaporated nickel particles that these are stable upto  $600^{\circ}\text{C}$  in air without lossing their selectivity. This makes the use of nickel grains very useful for photothermal conversion of solar energy.

### 1.7 Electrofloat Glasses

Electrofloat process involves the electric field induced ion-exchange of alkali containing glasses, one of the ion-exchange species being copper. The ion-exchanged glass is then subjected to a reduction treatment to precipitate the metallic particles. This process has been developed by Pilkington to produce the solar control coating.

### 1.8 Electro-conducting Glasses

#### 1.8.1 Metallic regime

A number of methods has been developed to obtain a highly conducting layer on or within the surface of the glass. These can be divided under two broad catagories. In the first, the layer is simply applied on to the surface of the glass.

Platinum, gold<sup>36</sup> or copper salts are heated to reduction on the surface, metals are vaporised on to the surface<sup>37</sup>, silver oxides and metal powders are fired on with the help of auxiliary fluxes and lacquers containing suspensions of flaky metals<sup>38</sup> are applied. The second catagory involves techniques

whereby various glasses containing lead oxide and other metal oxides are reduced in hydrogen gas to induce a conducting layer within the glass surface<sup>39,40</sup>.

Some alkali containing silicate glasses develop high surface conductivity<sup>41,42</sup> when they are subjected to an ion-exchange treatment followed by reduction. The process involves the dipping of the glass in molten silver nitrate at about 300°C for certain period of time so that alkali silver ion-exchange takes place. Then the glass is reduced in hydrogen gas in the temperature range of 250°C to 400°C so that silver metal atoms nucleate and grow to form the interconnected chains of metal and hence a highly conducting layer is induced within the surface of the glass. This is confirmed by electron microstructural analysis. The surface resistance is typically in the range of 0.15  $\Omega/\square$  to 4.1  $\Omega/\square$  depending on temperature and duration of the reduction treatment. It is found that prior to the thermo-chemical treatment it is necessary to make the glass surface sufficiently rough by grinding with 120 mesh silicon carbide powder to induce highly conducting layer. It is believed that the rough surface provides the potential sites for silver metal to nucleate and grow during the reduction treatment. It has been shown recently<sup>43</sup> that the ceramised  $\text{CaO-SiO}_2\text{-Na}_2\text{O-Bi}_2\text{O}_3$  systems develop high surface conductivity when they are ion-exchanged in molten silver nitrate followed by reduction in hydrogen gas. The typical surface resistance varies in the range

of  $0.08 \text{ } \Omega/\square$  to  $14.76 \text{ } \Omega/\square$  depending on the compositions and reduction temperature and time. The glass-crystal interface of the partially crystallised glass provides the potential sites for the silver metals to nucleate and grow during reduction treatment. Hence, surface roughness is not necessary in this process of generating highly conducting layer.

### 1.8.2 Dielectric regime

When oxide glass systems containing metals are melted under ordinary or reducing conditions, they develop a microstructure very similar to that of cermet films produced by sputtering or evaporation. Mixtures of oxides in the  $V_2O_5-P_2O_5$  system containing  $Ag_2O$  or  $Bi_2O_3$ <sup>44</sup>,  $Na_2O-B_2O_3-SiO_2$  system containing  $Bi_2O_3$  or pure selenium<sup>45</sup> and  $PbO-B_2O_3$  system<sup>46</sup> containing  $Bi_2O_3$  when melted and cooled rapidly induce precipitation of metallic granules of silver, bismuth or selenium in the corresponding glass matrix. The precipitated phases have been confirmed by selected area electron diffraction. The particle size found by electron microstructural analysis is of the order of a few hundred angstroms. Compared to base glasses the metal containing glasses show a decrease in resistivity. These glasses containing a distribution of metallic particles show semiconducting behaviour. From the temperature dependent conductivity measurements it has been concluded that the mechanism involved is the tunnelling of electrons between conducting metallic islands<sup>45,47</sup>.

The borosilicate system<sup>48</sup> containing  $\text{Bi}_2\text{O}_3$  and/or  $\text{Ag}_2\text{O}$  have been melted in a reducing condition. Fibres have been drawn from single hole bushing made of pure  $\text{Al}_2\text{O}_3$ <sup>49</sup>, at a fiberising temperature of around  $1100^\circ\text{C}$ . The fibres are found to have a microstructure consisting of bismuth and/or silver metallic particles of sizes ranging from 100 to  $500 \text{ \AA}$ , dispersed in the glass phase. The conductivity is electronic in nature and the mechanism is found to be electron tunnelling between the conducting metallic species similar to what has been observed in the case of bulk glass-metal microcomposites.

### 1.9 Memory Switching

In certain amorphous systems, when an applied electric field to the sample crosses a certain critical value the sample goes from a high resistance state to a low resistance state. This phenomenon is known as switching. There are two types of switching - threshold and memory. When the applied electric field is removed the threshold switch reverts back to the off-state. On the other hand the memory switch remains in the on-state even after the removal of the electric field. Alkali borosilicate glasses containing bismuth oxide when subjected to ion-exchange in molten silver nitrate followed by a reduction in hydrogen are found to have microstructures consisting of metallic particles distributed in a glassy matrix. This system<sup>50</sup> is found to exhibit memory switching with a reduction of resistance of six orders of magnitude when the applied electric field

crosses the critical value of 30 V/cm. When a 5-volt pulse of 10 msec. duration is applied to the sample it goes from the off to the on-state. However, on application of a 50-volt pulse of 10  $\mu$  sec. duration the sample switches back to the off-state. These glasses have been evaporated in a vacuum of  $10^{-5}$  torr on to alumina substrates to form thin films of a few micron thickness. Such films<sup>51</sup> also show memory switching. When the sample in the on-state is heated above a temperature (around the melting point of bismuth metal) it reverts from the on to the off-state. Recently,  $V_2O_5$ - $P_2O_5$  glasses<sup>44</sup> containing metallic bismuth or silver have been reported to show memory switching. The memory switching action has been explained on the basis of a particle stretching model.

#### 1.10 High Strength Glasses and Fibres

Alkali borosilicate glass fibres<sup>48</sup> containing bismuth and/or silver are found to have higher strength compared to those drawn from the base glass composition. However, the improvement is small. This increase in strength is believed to arise due to the deflection of cracks along the glass-metal interface during the course of crack propagation<sup>52</sup>. All fibres containing metallic silver particles are found to have higher Young's moduli compared to the base glass fibres. This arises due to a higher modulus of silver.  $SiO_2$ - $B_2O_3$ - $K_2O$ - $Al_2O_3$ - $As_2O_3$ <sup>53</sup> glasses containing silver are found to have higher rupture moduli as obtained from the three point bending measurement compared to base glasses.

Similarly alkali aluminoborosilicate glasses<sup>54</sup> containing bismuth have higher rupture moduli and Young's moduli compared to base glasses.

#### 1.11 Present Work

Memory switching observed in silicate and vanadium phosphate glasses containing metallic granules of bismuth has been qualitatively explained as due to the stretching of these particles under the action of an electric field. The objectives of the present thesis are the following :

1. To develop a detailed model to explain quantitatively the memory action in oxide glasses containing microgranules of metallic bismuth, specifically to calculate the threshold field as a function of different microstructural parameters.
2. To compute the current-voltage characteristics of these systems using this model especially in the negative resistance region.
3. To estimate the switching time for different microstructural configurations.
4. To carry out suitable experimental measurements to test the validity of the model.
- 5(a) To undertake detailed optical characterization of these glass-metal composites.
- (b) To apply the different models of inhomogeneous media to explain the optical absorption data.

## CHAPTER 2 \*

### PARTICLE STRETCHING MODEL AND THRESHOLD FIELD IN VANADIUM PHOSPHATE AND SILICATE GLASSES CONTAINING BISMUTH GRANULES

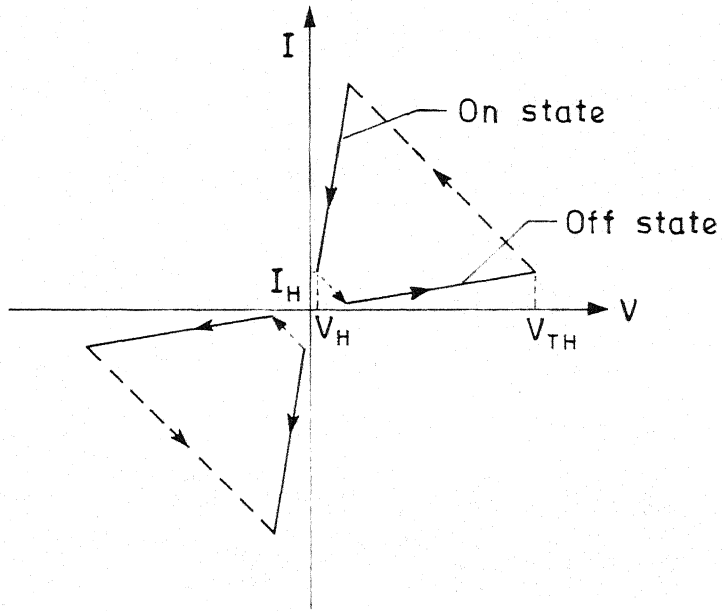
#### 2.1 Introduction

Preliminary reports on switching in chalcogenide glasses first appeared in the literature nearly two decades ago<sup>55,56</sup>. Ovshinsky's paper<sup>57</sup> in 1968 described the prototype of a reliable potential device and subsequently extensive theoretical and experimental investigation have been undertaken in various laboratories to understand the phenomenon. The switch described by Ovshinsky is a sputtered film of a typical thickness of about 1  $\mu\text{m}$  sandwiched between two metal or graphite electrodes. The material used is an amorphous semiconductor with an activation energy  $\sim 0.5$  eV and optical band gap  $\sim 1.0$  eV<sup>58</sup>. The physical properties of these materials have since been widely discussed in literature<sup>59-66</sup>.

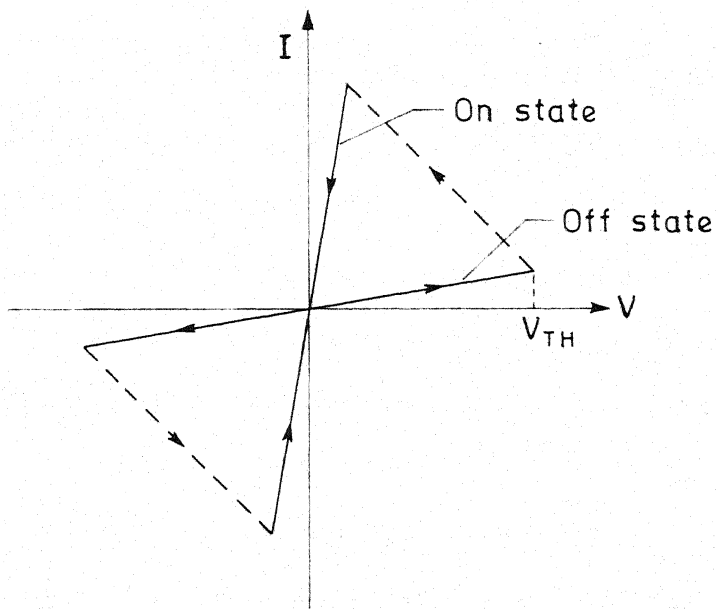
Switching can be of two types - threshold and memory. Figures 2.1(a) and 2.1(b) show the schematic representations of I-V characteristics of a threshold and a memory switch respectively. Both of these switches go from a high resistance state (off-state) to a low resistance state (on-state) via

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\* A paper based on this work has been published in J.Appl.Phys. 51, 3896 (1980).



(a)



(b)

Fig. 2.1 Schematic representations of I-V characteristics of (a) threshold (b) memory switch.



negative resistance when the applied electric field crosses a critical value. This is denoted as  $V_{TH}$  in figure 2.1. In contrast to the threshold switch, a memory switch remains in the on-state even after the removal of the applied field. However, a minimum holding current  $I_H$  is required to retain the on-state of the threshold switch. When the applied field is removed, the threshold switch returns to the off-state. A strong electrical pulse with short duration is required to bring the memory switch from the on-state to the off-state.

Whether a chalcogenide glass exhibits threshold or memory switching is primarily determined by its composition<sup>67</sup>. A typical threshold composition is  $As_{30}Te_{48}Si_{12}Ge_{10}$  (the so-called STAG glass)<sup>57</sup>. Usually most of the memory compositions are close to  $Ge_{15}Te_{81}X_4$  (X being As, S, Sb etc. or a combination<sup>68,69</sup>). The composition dependent switching characteristics of chalcogenide glasses can be understood qualitatively from their glass forming ability. The glass forming regions in the two ternary systems Ge-Te-As and Si-Te-As have been experimentally determined<sup>70,71</sup>. From these Owen et al.<sup>67</sup> have delineated the glass forming region of four component system, Ge-As-Te-Si by interpolation. It is reported that the so-called STAG glass falls at the centre of the glass forming region and hence the STAG glasses are resistant to crystallisation. On the otherhand the memory glass composition  $Ge_{15}Te_{81}As_4$  falls near the edge of the glass forming boundary. So they easily get crystallised

above the glass transformation temperature ( $T_g$ ) but at the same time can be quenched quickly from molten state to form glass. Thus the choice of memory composition should be a balance between the ease of crystallisation above  $T_g$  and tendency to glass formation. The threshold composition should be such that it makes the glassy state as stable as possible.

Two types of theories - thermal and electronic have been proposed to explain the switching behaviour. The classification depends on whether the on-state is achieved by heating (thermal model) or by non-equilibrium enhancement of carriers (electronic model). In the thermal model, the application of voltage across the sample causes the temperature to rise to a critical value due to Joule heating. After a certain time when the critical temperature is exceeded no stable temperature distribution is possible and any fluctuation causes the temperature to rise very fast until an upper limit, set by the external circuit resistance, is reached<sup>72</sup>. The result is the formation of the hot conducting channel in the on-state and the associated negative resistance state prior to switching. Earlier investigations on thermal instability have been reported by Lueder et al.<sup>73</sup> and Ridley<sup>74</sup>. Recently, many authors<sup>67,72,75-80</sup> have applied the thermal model to explain the threshold switching characteristics. Some authors<sup>67,79,80</sup> have also incorporated the field dependent conductivity along

with the temperature dependence to explain the switching characteristics in chalcogenide glasses.

According to the thermal model, the system returns to the off-state when the slope of I-V characteristics of the sample is equal to that determined by the load line of the circuit. Therefore, depending on the value of the external resistance the cut-off points should vary. Indeed this is observed by Hughes et al.<sup>81</sup>. The sample studied is a thick film. On the other hand Esquda et al.<sup>82</sup> have observed no matching of slopes for thin samples. A system where switching is possibly caused by the thermal mechanism is the vanadate glass system studied by Higgins et al.<sup>83</sup>. The switching in these glasses is attributed to a metal-insulator transition at 68°C.

The electronic model was first proposed by Mott<sup>84</sup> and Henisch<sup>85</sup>. The theory states that in the on-state sufficient double injection of carriers takes place to ensure the presence of degenerate electron and hole gas. The carrier density is  $\sim 10^{18}/\text{c.c.}$  and the Fermi energy of both carriers lies on the extended side of the respective mobility edge<sup>86</sup>. Thus the potential drop across the sample is small and obviously the holding voltage is slightly greater than the mobility gap. A number of authors<sup>87-92,58</sup> have used the electronic model to explain the chalcogenide switching characteristics.

To maintain the high density of electron and hole gas in the on-state, the supply of carriers should be there to

balance the loss of carriers by recombination and by diffusion out of the glass sample. Thus the minimum holding current represents the condition when the replacement of carriers fails to balance the loss and so the switch changes from the on-state to the off-state<sup>58</sup>.

In memory switching the on-state is induced by the precipitation of the conducting crystals in the glass system. Ovshinsky et al.<sup>93</sup> have shown that strong illumination can induce a similar behaviour. Fritzsche et al.<sup>94</sup> have observed by calorimetric measurement that there exists an exothermic peak between 200<sup>o</sup>-300<sup>o</sup>C and an endothermic peak at higher temperature for chalcogenide glasses showing memory switching. Therefore it is not entirely clear whether the crystallisation is induced by heating or by a high density of carrier injections<sup>86</sup>. To bring the memory switch from the on-state to the off-state a high amplitude pulse with short duration is applied such that the crystals get melted and quenched to the glassy state.

As described in Section 1.9 of Chapter 1, alkali borosilicate glasses containing bismuth show memory switching after ion-exchange<sup>50</sup> and reduction. It has recently been reported that V<sub>2</sub>O<sub>5</sub>-P<sub>2</sub>O<sub>5</sub> glasses containing bismuth and silver<sup>44</sup> and the evaporated thin films of alkali borosilicate glass containing bismuth<sup>51</sup> show memory switching. The typical switching field is of the order of 10<sup>4</sup> V/cm. Unlike the chalcogenide glasses

where memory switching is explained by crystallisation of glassy phase, the memory switching in glass-metal composite systems<sup>44</sup> has been explained qualitatively on the basis of particle stretching model. The model essentially states that if the metallic particles are in molten condition, the application of an electric field causes the particles to stretch which is being opposed by a surface tension force. Thus a critical electrical field causes the particles to stretch and form interconnected chains thereby forming a low-resistance on-state. So, in this chapter we shall develop this model to predict quantitatively the critical field for switching in the glass-metal micro-particulate system mentioned above.

## 2.2 Theoretical Model

When an electric field  $\vec{E}$  is applied to a dielectric matrix containing uniformly distributed metallic particles, the field induces opposite charges on the surface of the conducting species. If these metallic particles are in a molten state, two forces acting opposite to each other are operative. One is the coulombic attraction arising between two oppositely charged neighbouring metallic grains. This attraction force tends to stretch the molten metallic granules. The other is the surface tension force which opposes the stretching force<sup>95</sup>. Therefore, depending on the magnitude of the applied field an equilibrium will be reached when the two forces balance each other. The threshold field then corresponds to the situation when two

neighbouring grains touch each other. We assume that the metallic particles are spherical in shape in accordance with the experimental observation. Further we make the following assumptions for the simplicity of calculation :

- 1) The electric field is uniform throughout the matrix and is normal to the electrodes.
- 2) When the molten sphere is stretched it becomes ellipsoidal with major axis forming the axis of revolution.

### 2.2.1 Determination of electrostatic stretching force. $F_{el}$

To find the expression for the electrostatic force ( $F_{el}$ ) between the two polarised ellipsoids due to the presence of an electric field  $\vec{E}$ , the left hand ellipsoid is displaced by  $\delta x$  in the negative direction of x-axis as shown in figure 2.2. The work done against  $F_{el}$  is given by

$$\delta w = F_{el} \delta x. \quad (2.1)$$

This work is equal to the electrostatic energy stored in the volume ( $\delta v$ ) swept by the ellipsoid. Since electrostatic energy density is given by  $\frac{1}{2}\epsilon\epsilon_0 E^2$ ,

$$F_{el} \delta x = \frac{1}{2}\epsilon\epsilon_0 E^2 \delta v \quad (2.2)$$

where  $\epsilon$  and  $\epsilon_0$  are the relative dielectric permittivity of the glass-metal composite and the dielectric permittivity of free-space respectively.

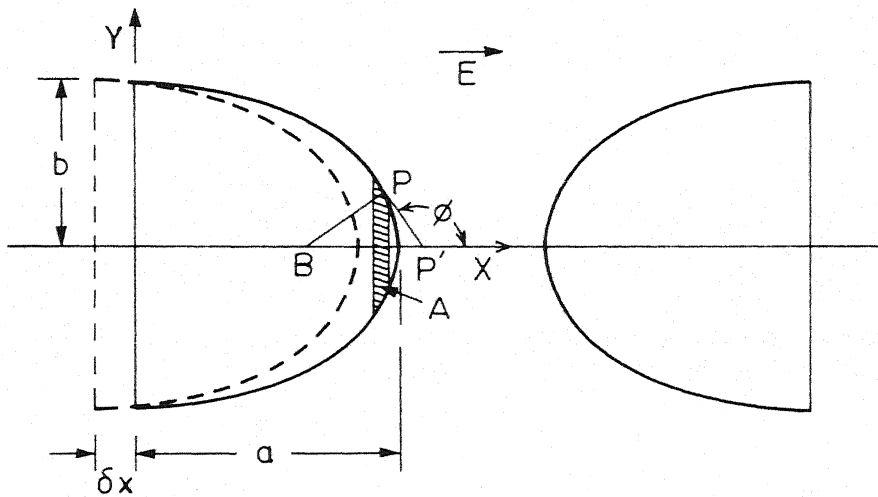


Fig. 2.2 Two metallic ellipsoids in an electric field.

### 2.2.1.1 Determination of volume $\delta v$

Let us consider an elemental circular strip of area  $dA$  at the point A in figure 2.2. The area  $dA$  is given by

$$dA = 2\pi y \sqrt{1 + y'^2} dx . \quad (2.3)$$

Due to the movement of strip by  $\delta x$  the volume ( $\delta v$ ) is given by

$$\delta v = dA \vec{n} \cdot \vec{i} \delta x \quad (2.4)$$

where  $\vec{n}$  and  $\vec{i}$  are the unit normal vector and unit vector along the x axis respectively.

For an ellipsoid with major axis as the axis of revolution  $\vec{n}$  is given by

$$\vec{n} = (\vec{i} \frac{x}{a^2} + \vec{j} \frac{y}{b^2} + \vec{k} \frac{z}{b^2}) / \sqrt{\frac{x^2}{a^4} + \frac{1}{b^2}(1 - \frac{x^2}{a^2})} \quad (2.5)$$

where, a and b are respectively the semi-major and semi-minor axes of the ellipse respectively.

Substituting  $dA$  and  $\vec{n}$  respectively from equations (2.3) and (2.5) in equation (2.4) and then integrating the resulting expression from  $x = 0$  to  $x = a$ , we get  $\delta v$  as follows :

$$\delta v = \pi b^2 \delta x \quad (2.6)$$

Substituting equation (2.6) in equation (2.2) and simplifying, we get,



$$F_{e1} = \frac{1}{2} \pi \epsilon \epsilon_0 E^2 b^2 \quad (2.7)$$

### 2.2.2 Determination of excess surface tension force $F_s$

A curved surface is characterised by two radii of curvature  $R_1$  and  $R_2$  which are given by the expressions,

$$1/R_1 = -y'' / (1+y'^2)^{3/2} \quad (2.8)$$

$$1/R_2 = 1/[y(1+y'^2)^{\frac{1}{2}}] \quad (2.9)$$

The excess pressure ( $\Delta P$ ) at point P on the ellipsoid (Fig. 2.2) is given by<sup>96</sup>,

$$\Delta P = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.10)$$

where  $\gamma$  is the surface tension of molten metallic particle.

The component of force along the x-axis acting on a circular strip passing through P is therefore given by

$$dF = \Delta P \, dA \, \vec{n} \cdot \vec{i} \quad (2.11)$$

After substituting  $R_1$  and  $R_2$  from equations (2.8) and (2.9) respectively in equation (2.10), the resulting  $\Delta P$  and  $dA$  and  $\vec{n}$  respectively from equations (2.3) and (2.5) are substituted in the equation (2.11). Then integrating the resulting expression from  $x = 0$  to  $x = a$ , we get the excess force  $F_s$  along the x-axis given by

$$F_s = 2\pi\gamma b \quad (2.12)$$

### 2.2.3 Determination of critical electric field

Figure 2.3 represents the situation when two grains of identical radius  $r$  are stretched into ellipsoidal shapes under the application of an electric field. The net surface tension force acting in a direction opposite to electrostatic force is given by

$$F_{ns} = 2\pi\gamma(r-b) \quad (2.13)$$

At equilibrium the electrostatic force  $F_{el}$  and the net surface tension force ( $F_{ns}$ ) must balance. Hence,

$$\frac{1}{2}\pi\epsilon\epsilon_0 E^2 b^2 = 2\pi\gamma(r-b) \quad (2.14)$$

Assuming that the volume of the particle remains unchanged after stretching, it can be shown that

$$b^2 = r^3/a \quad (2.15)$$

From figure 2.3 it can be shown that

$$a = r + (s_0 - s)/2 \quad (2.16)$$

Using equations (2.15) and (2.16) we get from equation (2.14) after simplification,

$$E^2 = \frac{4\gamma}{\epsilon\epsilon_0} \left[ r - \left( \frac{r^3}{r + (s_0 - s)/2} \right)^{\frac{1}{2}} \right] \cdot \left[ \frac{r^3}{r + (s_0 - s)/2} \right]^{-1} \quad (2.17)$$

The critical field (or switching field)  $E_m$  is defined as the field for which the two ellipsoidal particles touch each other in equilibrium. So by putting  $s = 0$  in expression (2.17), we get the critical field  $E_m$ , given by

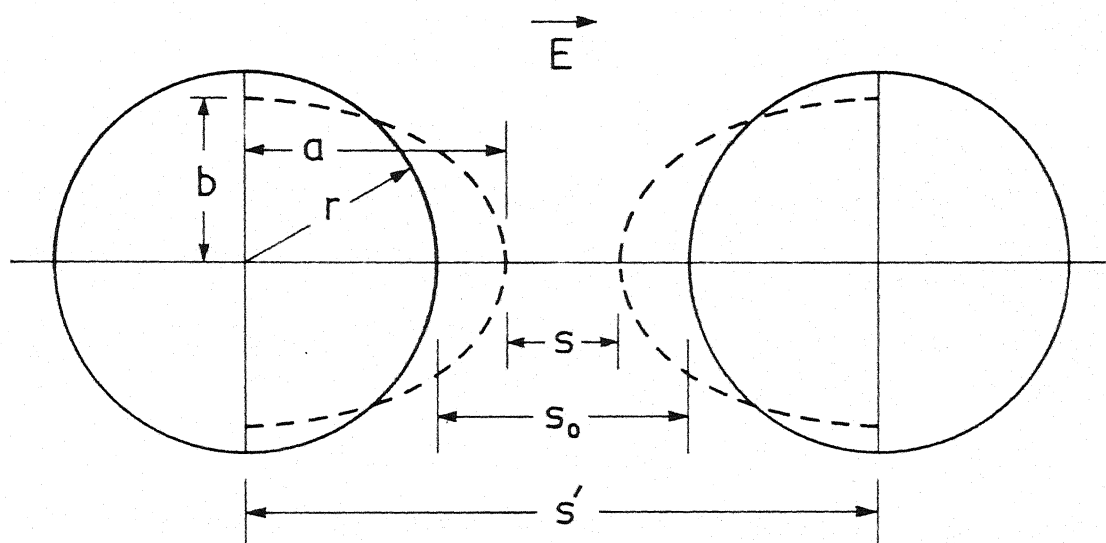


Fig. 2.3 Two metallic grains stretched into ellipsoidal shapes by an electric field.

$$E_m = \left\{ \frac{4\gamma}{\epsilon\epsilon_0 r} \left[ \left(1 + \frac{s_0}{2r}\right) - \left(1 + \frac{s_0}{2r}\right)^{\frac{1}{2}} \right] \right\}^{\frac{1}{2}} \quad (2.18)$$

#### 2.2.4 Solution of one dimensional heat equation

$E_m$  has been derived on the assumption that the metallic particles are in the molten state. In our model the temperature rise of the metallic species is brought about by Joule heating. For delineating the corresponding temperature profile, within the sample we consider the following one dimensional heat equation :

$$\frac{d^2 T}{dx^2} = - \frac{\sigma}{\kappa} E^2 \quad (2.19)$$

where  $\sigma$  be the electrical conductivity and  $\kappa$  is the thermal conductivity and  $T$  is the temperature in degree Kelvin.

The boundary conditions are :

$$T = T_{\text{exp}} \quad \text{at} \quad x = 0,$$

and

$$T = T_{\text{exp}} \quad \text{at} \quad x = l$$

where  $l$  is the thickness of the sample and  $T_{\text{exp}}$  is the temperature at which the experiment is carried out<sup>97</sup>. It has been established<sup>45</sup> for the silicate system under consideration that the electrical conduction takes place due to electron tunnelling between the metallic particles. So, we have taken the expression, for high field conductivity<sup>47</sup> as given by

$$\sigma_H = \left\{ \sigma_{\infty}(T) \exp(-E_0/E) \int_{-E_0/E}^{\infty} dz \, z \right\} \cdot \left\{ \exp(-z) / \left[ 1 - \exp\left(-\frac{z}{z + E_0/E} \cdot \frac{E_{c0}}{E_0 kT}\right) \right] \right\} \quad (2.20)$$

where  $\sigma_H$  is the high field conductivity and  $k$  is the Boltzmann constant.  $\sigma_\infty$  and  $E_0$  and  $c_0$  are given by,

$$\sigma_\infty = e^2 l' \gamma' / [(s_0' + d_0')^2 (2 \times s_0' + 1)^2 h] \quad (2.21)$$

$$E_0 = c_0 / e(s_0' + d_0') \quad (2.22)$$

$$c_0 = x s E_c^0 (1 + \frac{1}{2 \times s_0'}) \quad (2.23)$$

where  $l'$  be the recombination length,  $\gamma'$  be the geometric factor,  $s_0'$  be the most probable separation between the two metallic grains of diameter  $d_0'$ ,  $e$  be the electric charge,  $x$  is a constant,  $h$  is the Planck's constant,  $s$  be the separation between the two metallic granules and  $E_c^0$  is the energy required to generate a pair of fully dissociated positively and negatively charged metallic grains.

For  $V_2O_5$ - $P_2O_5$  glass system the temperature dependent conductivity has been taken as<sup>44</sup>,

$$\sigma = \sigma_0 \exp(-\phi/kT) \quad (2.24)$$

where  $\phi$  is the activation energy.

The heat equation (2.19) is nonlinear and no analytical solution is available. Therefore, it has been solved numerically.

### 2.2.5 Numerical solution

Equation (2.19) has been normalised, by putting  $y = x/l$  as follows :

$$\frac{d^2 T}{dy^2} = - \frac{1^2}{\kappa} \sigma E^2 \quad (2.25)$$

The boundary conditions in this case become

$$T = T_{\text{exp}} \quad \text{at } y = 0$$

and

$$T = T_{\text{exp}} \quad \text{at } y = 1 .$$

Fourth order Runge-Kutta-Nyström<sup>98</sup> method has been used to solve equation (2.25). The normalised length has been divided into 10 equal parts with a step length  $h' = 0.1$ . To use the Runge-Kutta-Nyström method for second order differential equation, it is necessary to know the functional value and the first derivative at the same point. Since, in our case, we know only the functional values but not the first derivative, so to start with a trial value of slope at the boundary has been assumed. In the case of silicate system, the conductivity expression (2.20) involves the integration and this has been evaluated by using Simpson 1/3 rule<sup>99</sup>. After computing the temperature distribution, we have compared the computed temperature at  $h' = 1$  with the boundary value at  $h' = 0$ . Depending on whether the computed temperature at  $h' = 1$  is greater or less than the temperature at  $h = 0$ , the trial value of slope is reduced or increased respectively. This process is continued until we get two slopes in subsequent iterations such that in one case the computed temperature at  $h' = 1$  is greater than the

boundary value and in the other case the temperature at  $h' = 1$  is less than the same. By using Regula-Falsi method, we have computed the temperature distribution, within an error of  $\pm 0.1^\circ\text{K}$ . The same technique has been used for a particular value of electric field to find the thickness within  $\pm 0.1 \mu\text{m}$  error such that the centre of the sample reaches the melting temperature of bismuth. The above scheme has been used to compute the temperature distribution for different combination of particle sizes, particle diameter to separation ratios, electric fields etc. In the computation the appropriate values of  $\kappa$  and  $\epsilon$  have been taken from references ([100], [44] and [45]). In the numerical computation of the temperature profile, the effect of particle size on the melting point of bismuth to be described in the following section, has been incorporated. The computer programme written in fortran language is given in Appendix 1.

### 2.2.6 Dependence of melting point on particle size

It has been observed experimentally<sup>101</sup> that the melting temperature of bismuth particle decreases as the particle size decreases. The implication of this in our model is that the applied electric field necessary to bring the metallic bismuth in the molten condition will be small for smaller particles. So the functional relation between the melting temperature and the particle size has been derived thermodynamically in the following section.

### 2.2.6.1 Derivation of particle size dependent melting point expression

Let  $\alpha$  and  $\beta$  in figure 2.4 denote the solid and the liquid phases respectively under equilibrium at the melting temperature  $T$  of the solid phase. In such a case, it can be shown that under constant pressure,

$$(S_{\beta} - S_{\alpha})dT = -(d\mu_{\beta} - d\mu_{\alpha}), \quad (2.26)$$

where  $S$  denotes entropy,  $\mu$  the chemical potential, and the subscripts indicate the phases.

For a transfer of  $dn_{\alpha}$  moles from  $\alpha$  to  $\beta$  phase, the Gibbs free energy change at constant temperature and pressure is given by

$$dG|_{T,P} = (\mu_{\alpha} - \mu_{\beta})dn_{\alpha} + \gamma(dA_{\alpha} + dA_{\beta}), \quad (2.27)$$

where  $dA_{\alpha}$  and  $dA_{\beta}$  represent the change of surface area in the two phases and  $\gamma$  is the surface energy (we assume that solid-liquid and liquid-matrix interfacial energies have the same value).

For the geometry assumed we can write

$$dA_{\alpha} = (2/r)\bar{V}_{\alpha} dn_{\alpha} \quad (2.28)$$

and

$$dA_{\beta} = 2\left(\frac{RdR}{R^2dR - r^2dr}\right)\bar{V}_{\beta}dn_{\beta}, \quad (2.29)$$



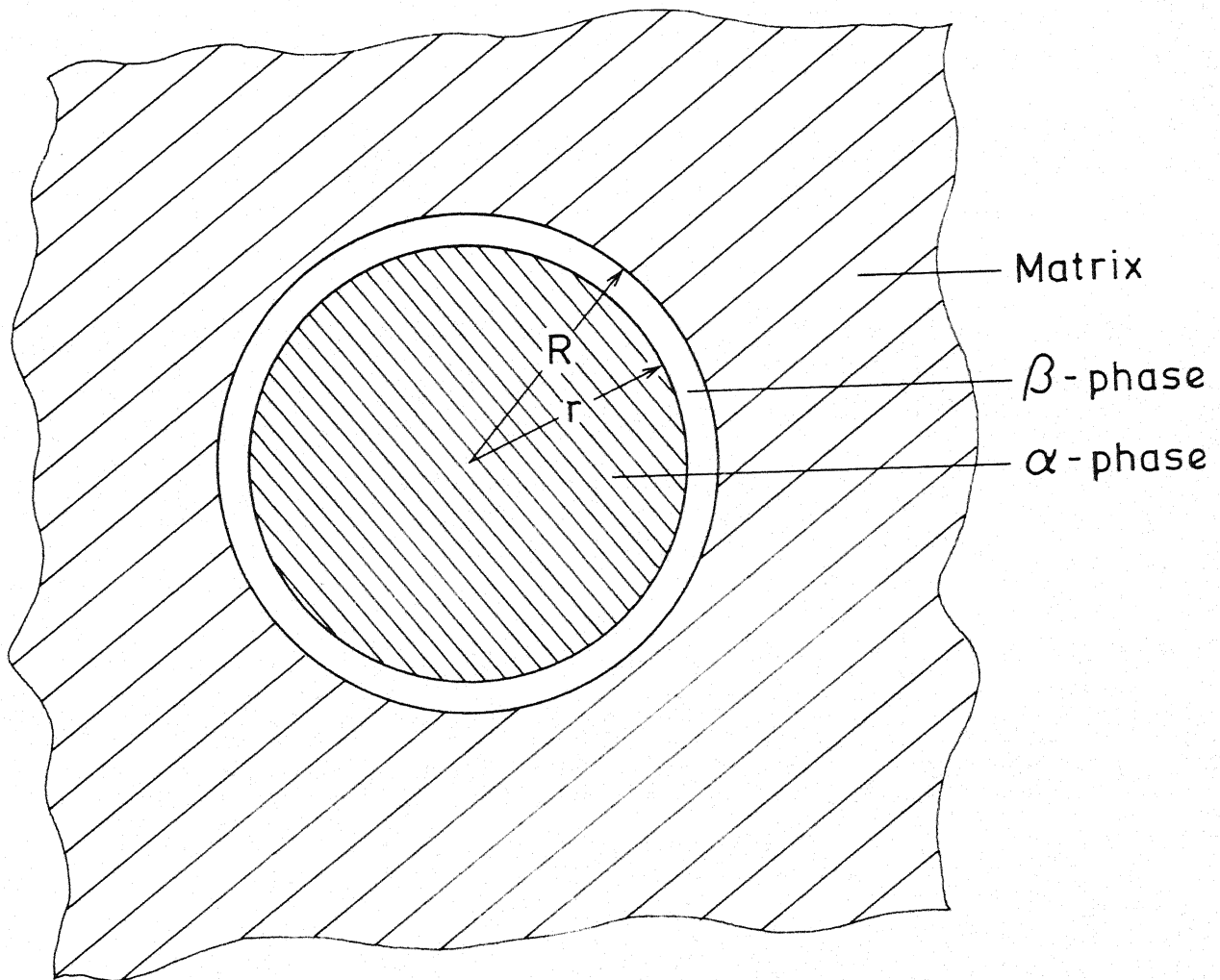


Fig. 2.4  $\alpha$  and  $\beta$  phases in equilibrium within a matrix.

where  $\bar{V}_\alpha, \bar{V}_\beta$  are the molar volumes of  $\alpha$  and  $\beta$  phases respectively. At the start of melting, we can assume  $R \approx r$  and equation (2.29) then becomes

$$dA_\beta = \frac{2}{r} \left( \frac{dR/dr}{(dR/dr)-1} \right) \bar{V}_\beta dn_\beta. \quad (2.30)$$

We can also write

$$4\pi r^2 dr \bar{V}_\beta / \bar{V}_\alpha = 4\pi R^2 dR, \quad (2.31)$$

where terms on both sides represent the change of volume of the  $\beta$  phase as a result of the transfer of  $dn_\alpha$  moles from the solid to the liquid phase. Assuming  $R \approx r$ , equation (2.31) simplifies to

$$dR/dr = \bar{V}_\beta / \bar{V}_\alpha. \quad (2.32)$$

Combining equation (2.30) and (2.32) we get

$$dA_\beta = \frac{2}{r} \left( \frac{\bar{V}_\beta^2}{\bar{V}_\beta - \bar{V}_\alpha} \right) dn_\beta. \quad (2.33)$$

Substituting equations (2.28) and (2.33) in equation (2.27) and using the relation  $dn_\alpha = -dn_\beta$ , we get

$$dG|_{T,P} = (\mu_\alpha - \mu_\beta) dn_\alpha + \frac{2\gamma}{r} \left( \bar{V}_\alpha - \frac{\bar{V}_\beta^2}{\bar{V}_\beta - \bar{V}_\alpha} \right) dn_\alpha. \quad (2.34)$$

At equilibrium,  $dG|_{T,P} = 0$ . Therefore from equation (2.34) we can write

$$d\mu_\beta - d\mu_\alpha = - \frac{2\gamma}{r^2} \left( \bar{V}_\alpha - \frac{\bar{V}_\beta^2}{\bar{V}_\beta - \bar{V}_\alpha} \right) dr. \quad (2.35)$$

For the transition from  $\alpha$  to  $\beta$  phase, we can write

$$\Delta H - T(S_\beta - S_\alpha) = 0, \quad (2.36)$$

i.e.,

$$S_\beta - S_\alpha = \Delta H/T,$$

where  $\Delta H$  is the molar heat of fusion. From equations (2.26), (2.35) and (2.36) we get,

$$\frac{\Delta H}{T} dT = \frac{2\gamma}{r^2} \left( \bar{V}_\alpha - \frac{\bar{V}_\beta^2}{\bar{V}_\beta - \bar{V}_\alpha} \right) dr. \quad (2.37)$$

Integrating between the limits from  $T_m$  (bulk melting point) to  $T$  and from  $r = \infty$  to  $r$  the following expression is obtained :

$$\ln \frac{T}{T_m} = - \frac{2\gamma}{\Delta H} \left( \bar{V}_\alpha - \frac{\bar{V}_\beta^2}{\bar{V}_\beta - \bar{V}_\alpha} \right) \frac{1}{r}. \quad (2.38)$$

The values for different parameters appearing in equation (2.38) have been taken from references ([102] and [103]).

### 2.2.7 Relation of computed fields to bulk field

The computed critical fields  $E_m$  and  $E_c$  are assumed to be related to the fields  $E_m^b$  and  $E_c^b$  respectively calculated on the basis of thickness by the following expressions,

$$E_m = (1 + d/s_o) E_m^b \quad (2.39a)$$

$$E_c = (1 + d/s_o) E_c^b \quad (2.39b)$$

where  $d$  and  $s_0$  are average particle diameter and inter-particle separation. This is justified because of the large value of  $\rho_{\text{glass}}/\rho_{\text{metal}}$  ratio<sup>47</sup>,  $\rho$  being resistivity.

### 2.3 Results and Discussions

Figure 2.5 is the plot of equation (2.38) showing the variation of the melting temperature of bismuth as a function of particle size. It is evident from the figure that the melting temperature decreases with the decrease in the radius of metallic particles. The implication is that for smaller particle sizes, the electric field necessary to reach the melting temperature of bismuth will be reduced.

Figure 2.6 shows a typical temperature profile as obtained by solving one dimensional heat equation (2.19). Open circles in the figure represent the bismuth in silicate system with the radius of bismuth particle 250 Å,  $E_c^b = 1.4 \times 10^3$  V/cm and  $s_0/d = 0.01$ . Closed circles represent bismuth in  $V_2O_5-P_2O_5$  system with radius of bismuth particle 400 Å,  $E_c^b = 0.4 \times 10^3$  V/cm and  $s_0/d = 0.01$ . The calculation is carried out at a temperature around 160°C so that the theoretically computed critical fields can be compared with the experimental results.

Figures 2.7 and 2.8 represent the bulk critical memory switching field  $E_m^b$  (equation 2.39a) as a function of different particle radii and separation to particle diameter ratios for bismuth in the silicate system and  $V_2O_5-P_2O_5$  system respectively.

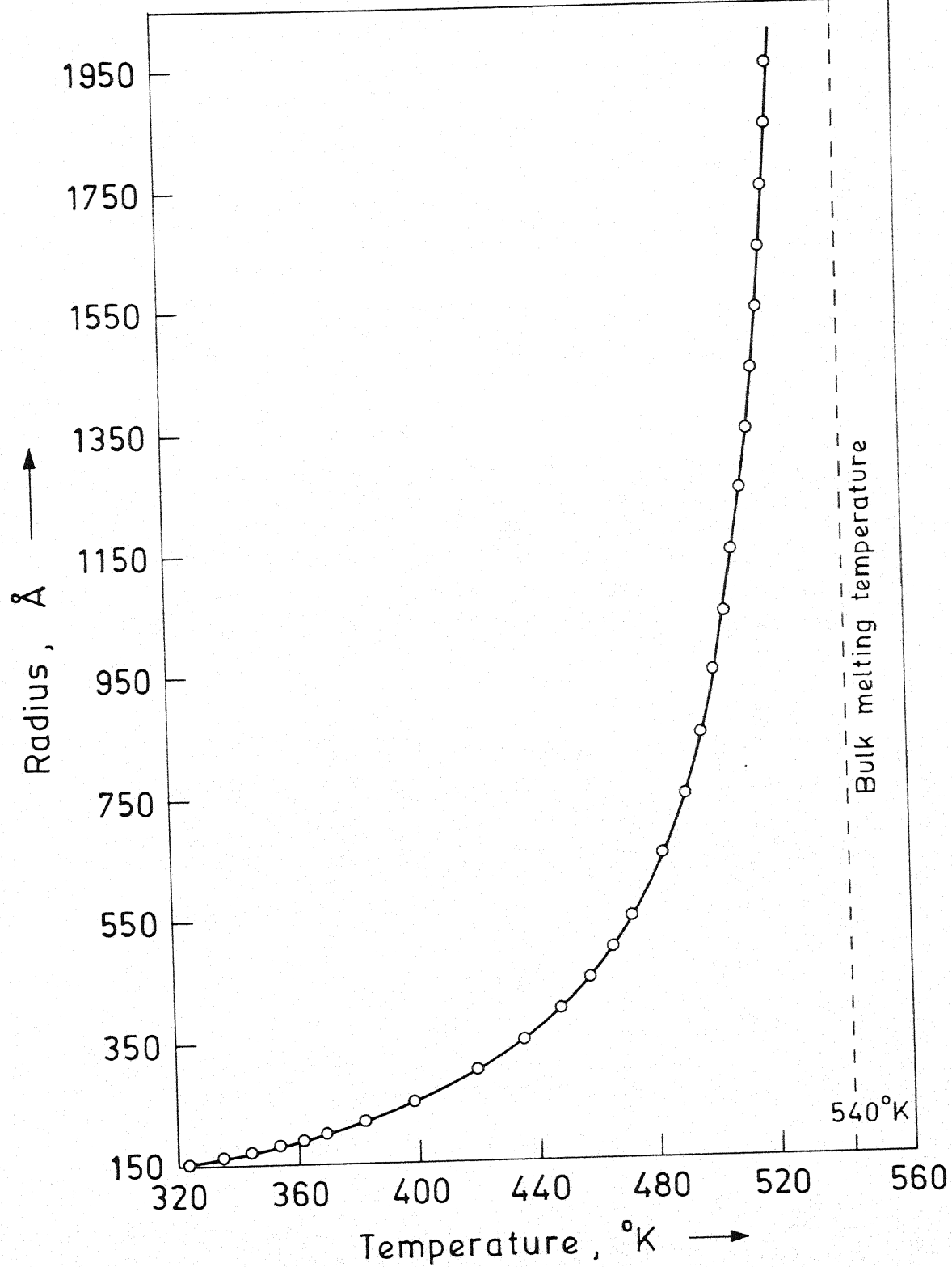


Fig. 2.5 Variation of melting temperature of bismuth metal as a function of particle radius.

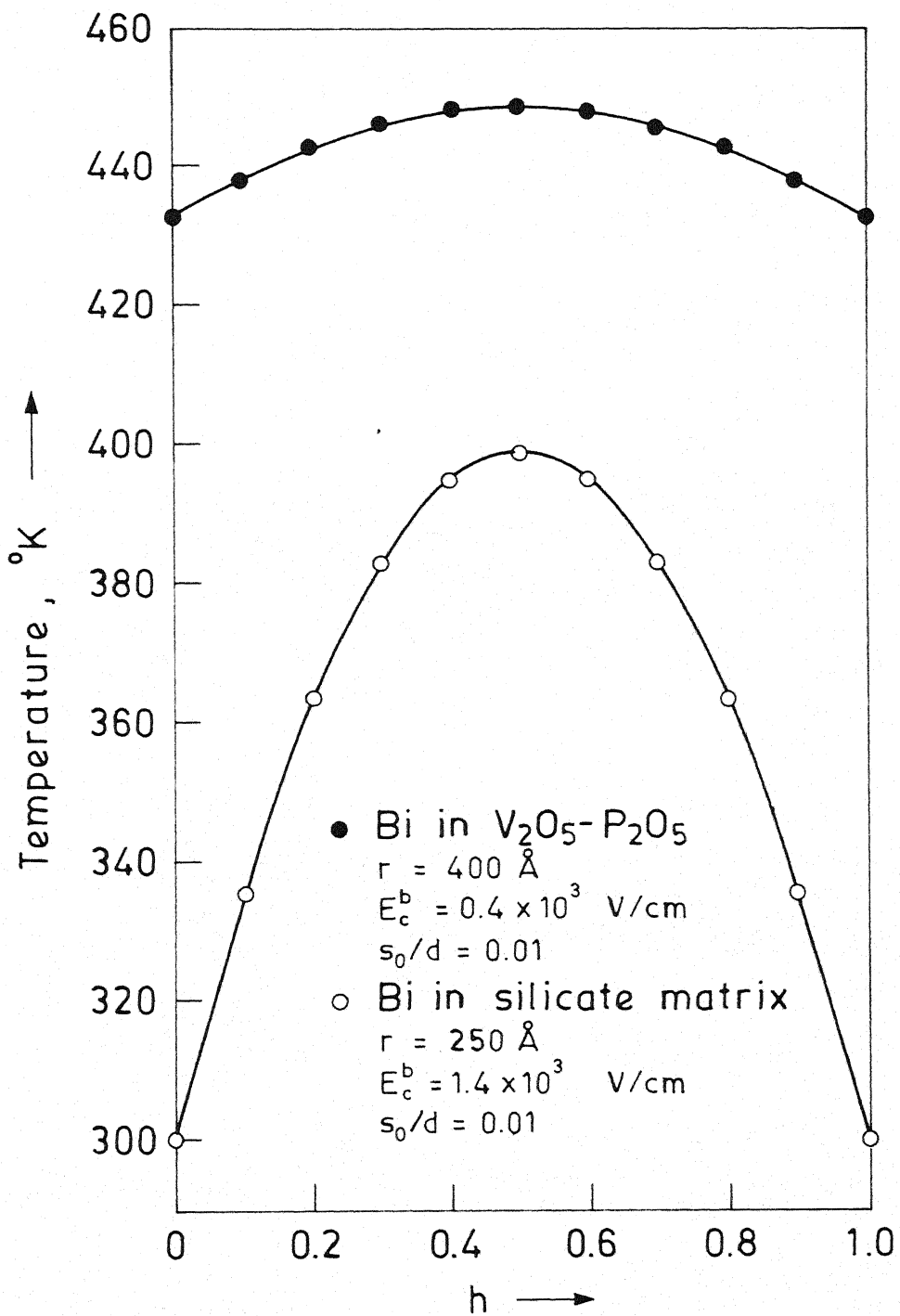


Fig. 2.6 Temperature profile from solution of one dimensional heat equation in a sample of thickness  $10 \mu\text{m}$ .

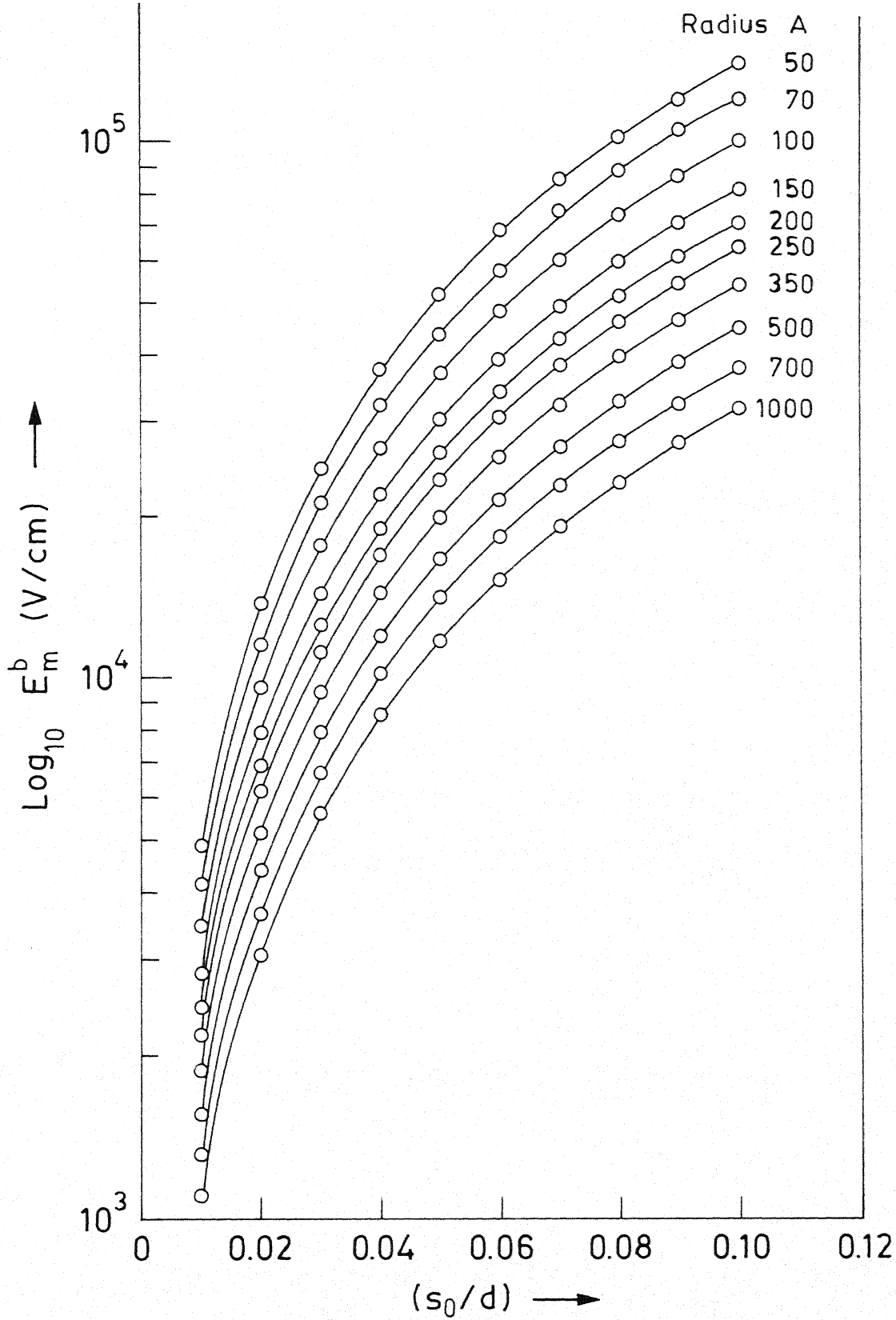


Fig. 2.7 Variation of critical field  $E_m^b$  as a function of  $(s_0/d)$  for different values of particle radius in silicate glass matrix.

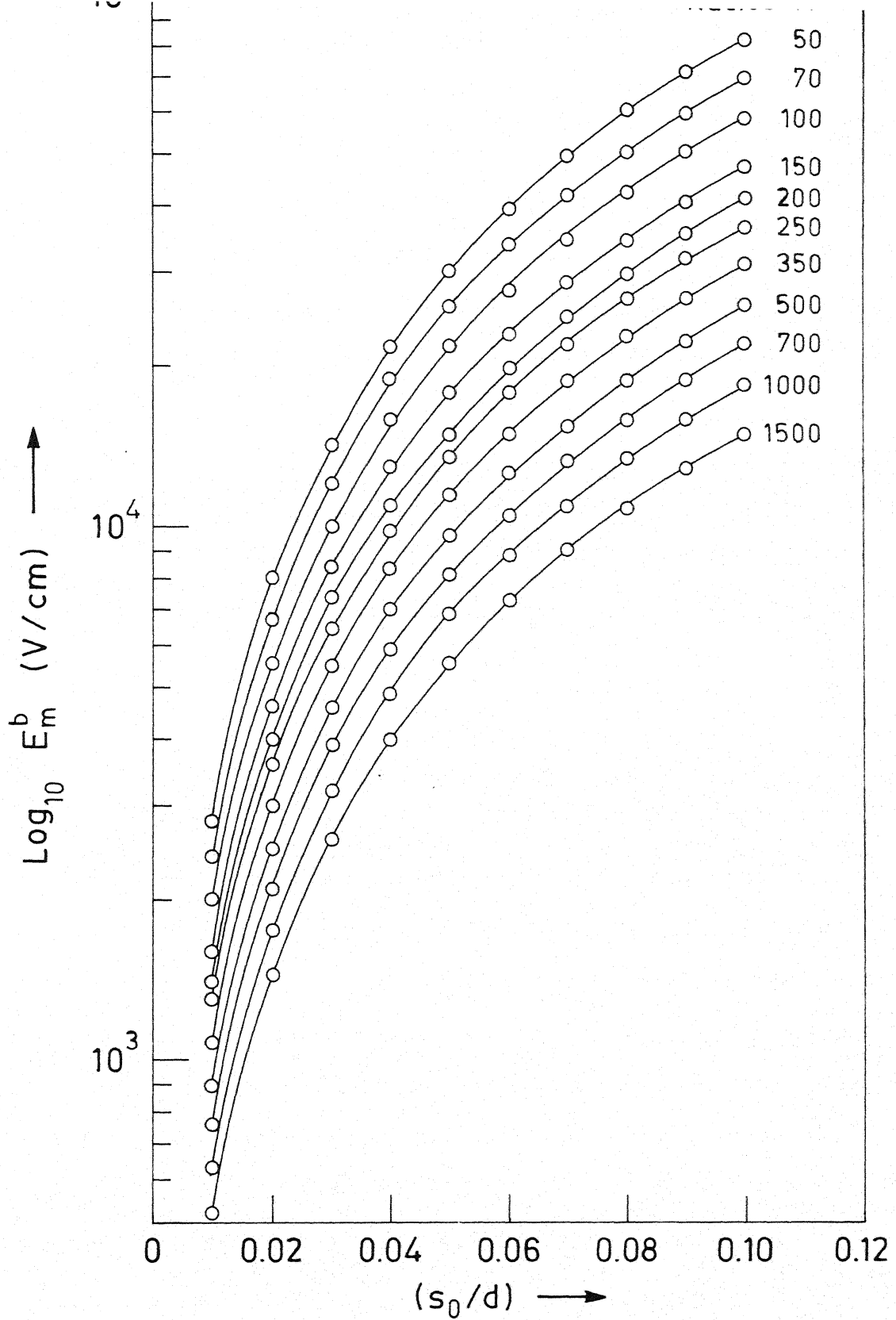


Fig. 2.8 Variation of critical field  $E_m^b$  as a function of  $(s_0/d)$  for different values of particle radius in  $V_2O_5$ - $P_2O_5$  glass matrix .



It is evident from figure 2.7 that the threshold field in silicate system varies over two orders of magnitude ( $10^3 - 10^5$  V/cm) for a particular value of particle radius as the  $s_0/d$  varies from 0.01 to 0.1. Similarly for vanadium phosphate glass (figure 2.8) the threshold field varies over two orders of magnitude ( $10^2 - 10^4$  V/cm) as  $s_0/d$  varies from 0.01 to 0.1. In table 2.1 values of critical field  $E_c^b$  for melting the metallic bismuth and field  $E_m^b$  needed for memory action are compared for different values of particle radii and separation to diameter ( $s_0/d$ ) ratios for a sample of thickness 10  $\mu\text{m}$ . It is observed that for parameters which can be realised in practice, the  $E_m^b$  is in general greater than  $E_c^b$ . It is, therefore, concluded that the threshold field for the systems under investigation will essentially be controlled by  $E_m^b$ .

In table 2.2 the threshold field values predicted by the present model are compared with the experimental results reported to-date for some silicate and vanadium phosphate glasses containing metallic bismuth. It is seen that the computed critical electric fields are of the same order of magnitude as observed experimentally. The agreement between these values are reasonable considering that we have made a number of simplifying assumptions in our analysis.

Table 2.1 Critical fields for melting ( $E_c^b$ ) and memory action ( $E_m^b$ ) in glass matrix containing bismuth granules

Particle Radius in Å	$s_0/d$	Specimen thickness = 10 $\mu m$	
		$E_c^b(V/cm) \times 10^{-3}$	$E_m^b(V/cm) \times 10^{-3}$
		$SiO_2-B_2O_3$ Matrix	$SiO_2-B_2O_3$ Matrix
		$V_2O_5-P_2O_5$ Matrix	$V_2O_5-P_2O_5$ Matrix
150	0.01	0.7	2.8
	0.03	2.1	14.5
	0.05	3.4	30.7
	0.07	4.5	50.0
	0.09	6.4	71.7
200	0.01	1.2	2.5
	0.03	3.4	12.6
	0.05	5.7	26.6
	0.07	8.0	43.3
	0.09	10.4	62.1
250	0.01	1.4	2.2
	0.03	4.1	11.2
	0.05	7.3	23.8
	0.07	9.5	38.7
	0.09	12.2	55.5
			1.6
			8.4
			17.7
			28.8
			41.4
			1.4
			7.2
			15.3
			25.0
			35.8
			1.3
			6.5
			13.7
			22.3
			32.0

300	0.01	1.5		2.0	1.2
	0.03	4.5		10.3	5.9
	0.05	7.4		21.7	12.5
	0.07	10.4		35.3	20.4
	0.09	13.4		50.7	28.3
350	0.01	1.6	0.2	1.9	1.1
	0.03	4.8	0.6	9.5	5.5
	0.05	7.9	1.0	20.1	11.6
	0.07	11.0	1.3	32.7	18.9
	0.09	15.0	1.7	46.9	27.1
400	0.01	1.7	0.4	1.7	1.0
	0.03	5.0	1.2	8.9	5.1
	0.05	8.2	2.0	18.8	10.8
	0.07	11.5	2.7	30.6	17.7
	0.09	15.2	3.4	43.9	25.3
450	0.01	1.7	0.5	1.6	1.0
	0.03	5.1	1.4	8.4	4.8
	0.05	8.4	2.4	17.7	10.2
	0.07	11.9	3.3	28.8	16.7
	0.09	15.8	4.2	41.4	23.9

contd..

500	0.01	1.8	0.6	1.6	0.9
	0.03	5.3	1.6	7.9	4.6
	0.05	8.6	2.6	16.8	9.7
	0.07	12.3	3.6	27.4	15.8
	0.09	16.2	4.6	39.3	22.7
550	0.01	1.8	0.6	1.5	0.9
	0.03	5.4	1.7	7.6	4.4
	0.05	8.8	2.8	16.0	9.2
	0.07	12.6	3.8	26.1	15.1
	0.09	16.5	4.8	37.4	21.6
600	0.01	1.8	0.6	1.4	0.8
	0.03	5.5	1.8	7.3	4.2
	0.05	9.0	2.9	15.3	8.9
	0.07	12.8	4.0	25.0	14.4
	0.09	16.8	5.0	35.8	20.7
650	0.01	1.9	0.6	1.4	0.8
	0.03	5.5	1.8	7.0	4.0
	0.05	9.1	2.9	14.7	8.5
	0.07	13.0	4.0	24.0	13.9
	0.09	17.0	5.1	34.4	19.9

contd....

700	0.01	1.9	0.6	1.3	0.8
	0.03	5.6	1.8	6.7	3.9
	0.05	9.3	3.0	14.2	8.2
	0.07	13.1	4.1	23.1	13.4
	0.09	17.2	5.2	33.2	19.2
750	0.01	1.9	0.6	1.3	0.7
	0.03	5.6	1.9	6.5	3.7
	0.05	9.4	3.0	13.7	7.9
	0.07	13.2	4.2	22.3	12.9
	0.09	17.3	5.3	32.1	18.5

Table 2.2 Comparison of theoretical and experimental switching fields

Glass Composition (mole % )	Maximum Diameter $\phi$	$E_m^b/\text{Exp}$ (V/cm)	$E_m^b/\text{Calc}$ (V/cm)
64SiO <sub>2</sub> , 18 B <sub>2</sub> O <sub>3</sub>	500	$1.2 \times 10^4$	$1.1 \times 10^4 (s_o/d=0.03)$
8 Bi <sub>2</sub> O <sub>3</sub> , 10 Na <sub>2</sub> O			$2.4 \times 10^4 (s_o/d=0.05)$ $3.9 \times 10^4 (s_o/d=0.07)$ $5.6 \times 10^4 (s_o/d=0.09)$
80V <sub>2</sub> O <sub>5</sub> , 15P <sub>2</sub> O <sub>5</sub>	800	$4.0 \times 10^3$	$1.0 \times 10^3 (s_o/d=0.01)$
5 Bi <sub>2</sub> O <sub>3</sub>			$2.8 \times 10^3 (s_o/d=0.02)$ $5.1 \times 10^3 (s_o/d=0.03)$ $7.8 \times 10^3 (s_o/d=0.04)$

## CHAPTER 3

### CURRENT-VOLTAGE CHARACTERISTICS OF VANADIUM PHOSPHATE GLASSES CONTAINING BISMUTH GRANULES

#### 3.1 Introduction

In Chapter 2, the threshold field for memory switching has been calculated in the case of glasses containing microgranules of bismuth dispersed in them. The I-V characteristics of the present systems of glass-metal composites show negative resistance region<sup>44,51</sup>. In the present chapter, the particle stretching model which has been developed in Chapter 2 has been used to compute the I-V characteristics of vanadium phosphate glasses containing bismuth, especially in the negative resistance region prior to the on-state as a function of particle diameters and particle separation to diameter ratios. The effect of specimen thickness on switching behaviour has been delineated both theoretically and experimentally. Also, the effect of temperature on the resistance of the samples in the memory state has been studied.

#### 3.2 Theoretical Consideration

##### 3.2.1 Calculation of I-V characteristics in the negative resistance region

The threshold field as calculated in Chapter 2 for memory action corresponds to the beginning of the negative resistance

region in the I-V plot of the glass-metal composite. According to the present model, initially within a portion of the sample at the centre where the temperature attains the value corresponding to the melting point of bismuth, elongated metal grains touch each other and thereby form a highly conducting region. Due to higher current flow more heat is generated and the conductive region grows from centre outwards. Such a regenerative process results in negative resistance characteristics and ultimately the system attains the highly conducting on-state.

For calculating the current-voltage (I-V) values in the negative resistance region we consider in figure 3.1 the situation within the specimen at some instant of time after the application of the critical switching field. In this figure  $l_m$  indicates the width of the conducting region (referred to as metallic region in subsequent discussion) where molten granular metal particles are interconnected and  $l_d$  represents the overall width of the remaining portion (referred to as dielectric region in subsequent discussion) of the sample. The resistance  $R_m$  of the metallic region is given by,

$$R_m = \rho_m \frac{l_m}{A} \quad (3.1)$$

where  $\rho_m$  is the resistivity of the specimen in the on-state. Experimentally observed  $\rho_m$  in the on-state has been used in the present analysis. A is the electrode area of the specimen.

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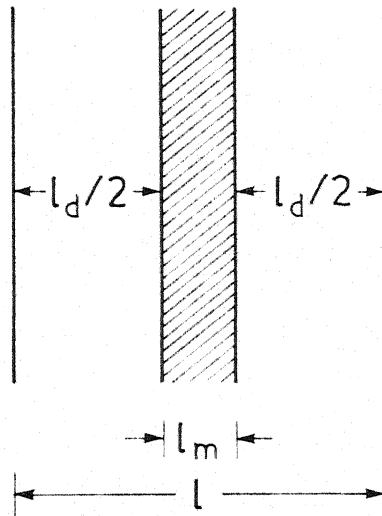


Fig. 3.1 Schematic representation of a glass-metal composite after the application of a critical field.

$l_m$  : width of metallic region

$l_d$  : width of dielectric region

Since resistivity of the glass-metal particulate system is dependent on temperature, to find the resistance of the dielectric region one has to take into account the temperature profile within the sample after the application of the critical electric field. The dielectric region has been divided into  $n$  equal parts each of width  $w$  so that the resistance  $R_d$  of this region is given by

$$R_d = \frac{w}{A} \sum_{i=1}^n \rho_{T_i} \quad (3.2)$$

where  $\rho_{T_i}$  denotes the resistivity of  $i$ th strip having a mean temperature  $T_i$  and

$$w = l_d/n \quad (3.3)$$

In our calculation we have chosen  $n$  suitably such that at every step of metallic region formation, the value of  $w$  is kept constant. The temperature distribution in the sample has been obtained by solving the time-dependent heat equation to be described in the following section. The resistivity has been evaluated from the equation (2.24) in Chapter 2. The pre-exponential factor and the activation energy have been obtained from experimental data of the present vanadium phosphate system containing bismuth<sup>44</sup>.

If the current passing through the circuit consisting of the sample and the series resistance  $R_s$  ohms be denoted by  $I_s$  amperes, we can write,

$$I_s = \frac{V_{app}}{R_m + R_d + R_s} \quad (3.4)$$

and

$$V_s = I_s(R_m + R_d) \quad (3.5)$$

where  $V_{app}$  is the applied voltage across the circuit.

For delineating the temperature profile within the sample, the rate of heat generation per unit volume needs to be evaluated. The latter is given by  $\sigma_d E^2$ , where  $\sigma_d$  is the conductivity of the specimen and  $E$  the electric field. However, after the onset of switching, in the present model, the sample consists of two regions viz. metallic and dielectric. The average values of field and conductivity to be used for computing the rate of heat generation per unit volume are therefore obtained as follows :

We can assume that after the coalescence of neighbouring metal granules near the specimen centre, the potential drop in the dielectric region occurs only in the glass matrix intervening the particles<sup>47</sup>. With this assumption, the effective field  $E_{eff}^d$  is then given by

$$E_{eff}^d = \frac{I_s R_d (s_o + d)}{l_d s_o} \quad (3.6)$$

where,  $s_o$  is the average interparticle separation and  $d$  the average diameter of metal particles.

Substituting  $I_s$  and  $R_d$  respectively from equations (3.4) and (3.2) in equation (3.6) we get,

$$E_{\text{eff}}^d = \frac{V_{\text{app}}(1 + (d/s_o)) \frac{W}{A} \sum_{i=1}^n \rho_{T_i}}{(R_m + R_s + \frac{W}{A} \sum_{i=1}^n \rho_{T_i}) l_d} \quad (3.7)$$

Similarly, the effective field,  $E_{\text{eff}}^m$  in the metallic region is given by,

$$E_{\text{eff}}^m = \frac{I_s R_m}{l_m} \quad (3.8)$$

From equations (3.1), (3.4) and (3.8) we can write,

$$E_{\text{eff}}^m = \frac{V_{\text{app}} \rho_m}{(R_s + R_s + \frac{W}{A} \sum_{i=1}^n \rho_{T_i}) A} \quad (3.9)$$

The average electric field  $E_{\text{av}}$  in the glass-metal particulate system at any time after the onset of switching is then given by,

$$E_{\text{av}} = (l_d E_{\text{eff}}^d + l_m E_{\text{eff}}^m)/l \quad (3.10)$$

The average conductivity  $\sigma_{\text{av}}$  is given by,

$$\frac{1}{\sigma_{\text{av}}} = \left( \frac{l_d}{\sigma_d} + \frac{l_m}{\sigma_m} \right) \frac{1}{l} \quad (3.11)$$

where  $\sigma_d$  and  $\sigma_m$  refer to the conductivities of the dielectric and the metallic region respectively.

The present analysis has been carried out with the applied field which corresponds to the critical field for memory action  $E_m$  given by the expression (2.18) in Chapter 2.  $E_m$  is related to the bulk field  $E_b$ , calculated on the basis of sample thickness by,

$$E_m = (1 + d/s_o)E_b \quad (3.12)$$

where

$$E_b = V_{app}/l \quad (3.13)$$

From equations (3.12), (3.13) and equation (2.18) of Chapter (2). We get

$$V_{app} = \left( \frac{1}{1+d/s_o} \right) \left\{ \frac{4\gamma}{\epsilon\epsilon_o r} \left[ \left( 1 + \frac{s_o}{2r} \right) - \left( 1 + \frac{s_o}{2r} \right)^{\frac{1}{2}} \right] \right\}^{\frac{1}{2}} \quad (3.14)$$

In the above expression,  $\epsilon, \epsilon_o, \gamma, r$  have the same meaning as given in Chapter 2. To find the expression for  $V_{app}$ , the voltage applied to the circuit, we have neglected the potential drop across the resistance in series with the sample. This is because of the fact that the magnitude of series resistance is orders of magnitude less than that of the sample in the off-state.

### 3.2.2 Numerical scheme for I-V computation

The normalised thickness is divided into ten equal parts and the grid points are denoted by 1,2, ..., 11 respectively. First of all the resistance of the sample is calculated from equation (3.2) corresponding to ambient temperature. From equations (3.4), (3.5) and (3.14) the potential drop and the current passing through the sample are then evaluated. These correspond to the starting point of the negative resistance region. In our calculation, we have neglected the temperature rise, due to Joule heating in the pre-switching region. The

time-dependent heat equation is then solved numerically to find a temperature distribution such that the sample centre (grid point 6) has attained the melting temperature of bismuth corresponding to the average particle size (equation (2.38), Chapter 2). Solution is then carried out corresponding to the time when the grid points 5 and 7 reach the melting temperature of bismuth. The molten particles in the region lying between the grid points 7 and 5 will be stretched forming the metallic region, because the electric field has the critical value. Values of  $R_m$  and  $R_d$  are then calculated corresponding to this state from equations (3.1) and (3.2) respectively. Substituting these in equations (3.4) and (3.5) the  $I_s$  and  $V_s$  values are calculated. The values of  $E_{av}$  and  $\sigma_{av}$  are then estimated from equations (3.10) and (3.11) respectively, which are then used in the next step of the computation. This procedure is repeated and  $I_s, V_s$  values are found at every step till we come to the one which involves the pair of grid points 2 and 10 respectively. The latter give the last but one point in the negative resistance region. The final point corresponds to the situation when the entire sample forms the metallic region thereby attaining the on-state.

### 3.2.3 Relaxation of temperature

To explain the threshold switching behaviour of the thick sample, as we shall see later, it is necessary to calculate the time required for the temperature at the centre of the sample

to go below the melting point of bismuth after the applied electric field is reduced to zero. The relaxation time ( $\tau$ ) is defined as the time which elapses after the removal of the electric field for the on-state temperature at the centre of the sample to attain the melting temperature of bismuth. The decay of temperature distribution in a rectangular slab after normalisation with respect to thickness is given by,

$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho' c l^2} \frac{\partial^2 T}{\partial x^2} \quad (3.15)$$

where  $\kappa$ ,  $\rho'$  and  $c$  respectively denote thermal conductivity, density and specific heat respectively.

The boundary conditions are :

$$T(0,t) = T(1,t) = 0 \quad (3.16)$$

$$T(x,0) = f(x) \text{ for } 0 \leq x \leq 1$$

where  $f(x)$  is the temperature distribution within the sample when it attains the on-state.

Solution of equation (3.15) is given by<sup>98</sup>

$$T(x,t) = \sum_{n=1}^{\infty} [ B_n e^{-\lambda_n^2 t} \sin(n\pi x) ] \quad (3.17)$$

$$\text{where, } \lambda_n = \frac{n\pi}{l} \left( \frac{\kappa}{\rho' c} \right)^{\frac{1}{2}} \quad (3.18)$$

and

$$B_n = 2 \int_0^1 f(x) \sin(n\pi x) dx \quad (3.19)$$

The solution of equation (3.17) has been worked out numerically, since only numerical values of temperature distribution function  $f(x)$  are known in the on-state.

### 3.2.4 Numerical solution

#### 3.2.4.1 Numerical solution of time dependent heat equation

The time dependent heat equation which is solved to find the temperature distribution within the sample for computing the I-V characteristics in the negative resistance region is given by

$$\rho'c \frac{\partial T}{\partial t^*} = \kappa \frac{\partial^2 T}{\partial y^2} + \sigma(T)E^2 \quad (3.20)$$

The boundary conditions are :

$$T(y) = T_{\text{exp}} \text{ for } 0 \leq y \leq 1 \quad \text{at } t^* = 0$$

$$T(0) = T(1) = T_{\text{exp}} \quad \text{at } t^* > 0$$

For ease of numerical computation, the equation (3.20) has been normalised with respect to thickness and for some time  $t_1$  by setting  $x = y/1$  and  $t = t^*/t_1$  and the normalised equation becomes,

$$\frac{\rho'c}{t_1} \frac{\partial T}{\partial t} = \frac{\kappa}{1^2} \frac{\partial^2 T}{\partial x^2} + \sigma(T)E^2 \quad (3.21)$$

The boundary conditions become ,

$$T(x) = T_{\text{exp}} \text{ for } 0 \leq x \leq 1 \quad \text{at } t = 0$$

$$T(0) = T(1) = T_{\text{exp}} \quad \text{at } t > 0$$



For solving equation (3.21) we have used Crank-Nicolson implicit finite difference formula<sup>104</sup>. The advantage of implicit finite difference scheme is that it gives unrestricted stability for  $p/h^2$  ratio<sup>105</sup>, where  $p$  and  $h$  are respectively the step lengths in time and  $x$  direction. So we have chosen a step length  $p = 0.1$  and  $h = 0.1$  in our computation.

In Crank-Nicolson implicit formula the time derivative is replaced by forward difference and the second order derivative in the  $x$  direction is replaced by a weighted sum of second order central difference at  $t$  and  $t+p$ . Applying these to equation (3.21), we get after simplification the following finite difference formula at a particular time  $t$ ,

$$\begin{aligned}
 & -\frac{\kappa}{2h^2} T_{x-h,t+p} + \left( \frac{1^2 p^2 c}{t_1 p} + \frac{\kappa}{h^2} \right) T_{x,t+p} - \frac{\kappa}{2h^2} T_{x+h,t+p} \\
 & = \frac{\kappa}{2h^2} T_{x-h,t} + \left( \frac{1^2 p^2 c}{t_1 p} - \frac{\kappa}{h^2} \right) T_{x,t} + \frac{\kappa}{2h^2} T_{x+h,t} \\
 & \quad + 1^2 \sigma \left( \frac{T_{x,t+p} + T_{x,t}}{2} \right) E^2
 \end{aligned} \tag{3.22}$$

In equation (3.22) the conductivity has been evaluated at a mean temperature of  $T_{x,t+p}$  and  $T_{x,t}$ <sup>104</sup>. Writing equation (3.22) for all the grid points along the  $x$ -direction we obtain a (9x9) tridiagonal matrix. For finding the temperature distribution from the above equations the Gauss matrix iteration<sup>99</sup> has been used. It can be shown from the above (9x9) tridiagonal matrix that each diagonal element is greater than the absolute sum of

the corresponding off-diagonal elements. This satisfies the condition for convergence of Gauss iteration scheme.

The following steps are involved to calculate the temperature distribution at different time intervals and to compute the time necessary to reach the melting temperature of bismuth.

- Step 1 : A temperature distribution is assumed to start the Gauss iteration.  $t = 0$  and  $p = 0.1$  are set, and a value of  $t_1$  is assumed.
- Step 2 :  $\sigma$  is evaluated corresponding to time  $t$ .
- Step 3 : Temperature distribution is computed using  $\sigma$  as evaluated in step 2.
- Step 4 :  $\sigma$  is evaluated at the mean value of temperatures evaluated at time  $t$  and the temperatures evaluated in the last iteration.
- Step 5 : Temperature distribution is obtained using  $\sigma$  as evaluated in step 4.
- Step 6 : Steps 4 and 5 are repeated until the difference of temperature distributions between two successive iterations is less than  $0.1^\circ\text{K}$ . This gives the temperature distribution at time  $t+p$ .
- Step 7 :  $t = t+p$  is set and steps 2 to 6 are repeated till  $t = 0.9$ .
- Step 8 : The difference between the temperature at the centre of the sample and the melting point of bismuth is computed.

- Step 9 : Depending on whether the difference is positive or negative  $t_1$  is decreased or increased.
- Step 10: The value of  $t_1$  in step 1 is replaced by the new value of  $t_1$  of step 9.
- Step 11: Steps 1 to 10 are repeated until we get two values of  $t_1$  such that in one case the difference as evaluated in step 8 is positive and in the other case it is negative.
- Step 12: Using method of bisection new value of  $t_1$  is evaluated and  $t_1$  in step 1 is replaced by this new value of  $t_1$ .
- Step 13: Steps 1 to 8 and then step 12 are repeated until the difference as computed in step 8 is within  $\pm 1^\circ\text{K}$  and the time which is evaluated in step 12 is the required time.

The programme for the above numerical computation is given in Appendix 2.

#### 3.2.4.2 Numerical solution of temperature relaxation

The coefficient  $B_n$  (equation (3.19)) has been evaluated by using Simpson 1/3 rule using the numerical values of  $f(x)$ , the temperature distribution as obtained from the solution of time dependent heat equation for different particle diameters and separation to diameter ratios. Using the method of bisection, the relaxation time as defined in Section 3.2.3 has been evaluated numerically for thin as well as thick samples.

### 3.3 Experimental

#### 3.3.1 Preparation of glass

A glass batch of composition  $80\text{V}_2\text{O}_5, 15\text{P}_2\text{O}_5, 5\text{Bi}_2\text{O}_3$  (mole %) has been prepared from reagent grade chemicals.  $\text{P}_2\text{O}_5$  is added as  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{V}_2\text{O}_5$  and  $\text{Bi}_2\text{O}_3$  are introduced as their oxides. The mixture is melted in a pure  $\text{Al}_2\text{O}_3$  crucible at temperature of  $700^\circ\text{C}$  for half an hour. Then the molten glass is cast in an aluminium mold and annealed at  $100^\circ\text{C}$  for half an hour and left for furnace cooling.

#### 3.3.2 Sample preparation

##### 3.3.2.1 Preparation of thin film

The thin film of glass has been prepared as follows<sup>44</sup> : The liquid droplet of molten glass is collected by dipping a stainless steel tube in the crucible containing the molten glass. The droplet has been blown into a large bubble by passing an inert gas e.g. nitrogen/argon through the tube from the other end. The thin film samples are collected from the resulting glass bubble.

##### 3.3.2.2 Preparation of thick film

The bulk glass has been thinned by successively grinding and polishing in SiC powder. Since vanadium phosphate glasses are readily attacked by water, the grinding and polishing are carried out in the presence of acetone. Samples of thickness

a few hundred microns are prepared by this method and are termed thick films.

### 3.3.3 Differential thermal analysis (DTA)

The bulk sample is ground and then sieved out in the range of -14 mesh to 20 mesh. This particle size is large enough so that the effect of surface crystallisation can be neglected in DTA<sup>106</sup>. To the ground sample is added around 30% of calcined  $\text{Al}_2\text{O}_3$  to avoid sintering of the glass particles. The DTA has been carried out in a MOM Derivatograph Hungary, at a heating rate of  $7^\circ\text{C}/\text{minute}$ .

### 3.3.4 X-ray analysis

Both heattreated and virgin glasses have been used for X-ray studies. The heattreatment of sample has been carried out in a wire wound furnace at  $359^\circ\text{C}$  for a period of one hour. The glass sample is ground and sieved to get powder of size below 400 mesh. The X-ray diffraction pattern of the powdered sample has been taken using General Electric XRD 5 Diffractometer. The monochromatic radiation used is  $\text{Cu K}_\alpha$ . The interplanar spacings have then been calculated from the intensity vs  $2\theta$  plot of the diffraction pattern by using the relation,

$$2d_{hkl} \sin\theta = n \lambda \quad (3.23)$$

where  $d_{hkl}$ ,  $\lambda$  and  $\theta$  are the interplanar spacing, X-ray wavelength and the diffraction angle respectively.

### 3.3.5 Electron microscopic analysis

Electron microscopic analysis has been carried out for both heattreated and virgin glass samples. The electron microscopic sample has been prepared as follows : First, the sample is thoroughly ground in an agate mortar and then dispersed in acetone, so that the very fine particles, needed for transmission electron microscope remain in suspension. A few drops of acetone containing finely suspended glass particles is poured on the carbon coated electron microscope (EM) grid. One drop of collodion is then poured on deionised distilled water to form a very thin film of collodion. The EM grid containing the powdered glass sample is then put on the film so that the sample particles face the collodion film. Lastly, the EM grids are fished out by clean glass slides. The sample is, therefore, sandwiched between the carbon and collodion thin films. The electron microstructure and the selected area diffraction of the samples at 100 kV have been taken in a Phillips EM 301 Electron Microscope.

The diameters of the diffraction rings have been measured from the negative by using a graduated eye-piece with an accuracy of 0.1 mm. The interplanar spacings are calculated from the relation given below :

$$\text{Camera constant} = r d_{hkl} \quad (3.24)$$

where  $r$  is the radius of the diffraction ring and  $d_{hkl}$  the corresponding interplanar spacing. The camera constant has been determined from the standard gold diffraction pattern obtained at 100 kV.

### 3.3.6 Electrical measurement

The I-V characteristics of both thick and thin samples have been measured. The resistance of the thin film sample in the memory state has been measured as a function of temperature. To carry out the electrical measurement, the samples have been coated with gold to form electrodes. This has been done by evaporating pure gold in vacuum.

#### 3.3.6.1 Electrical circuit

Figure 3.2 represents schematically the electrical circuit used for measurements of I-V characteristics of different samples. The sample and the standard resistance are in series with a 30 Volts 2 amperes DC regulated power supply (Aplab, Model 7152). The potential drops across the sample and the standard resistance are fed to the X-axis and Y-axis of the X-Y recorder respectively (No. 2000 made by Digital Electronics Ltd., India). Hence, the plot on the X-Y recorder corresponds to the I-V characteristics of the sample. The same circuit has been used to measure the resistance of thin samples in the memory state as a function of temperature from 23°C to about 100°C.

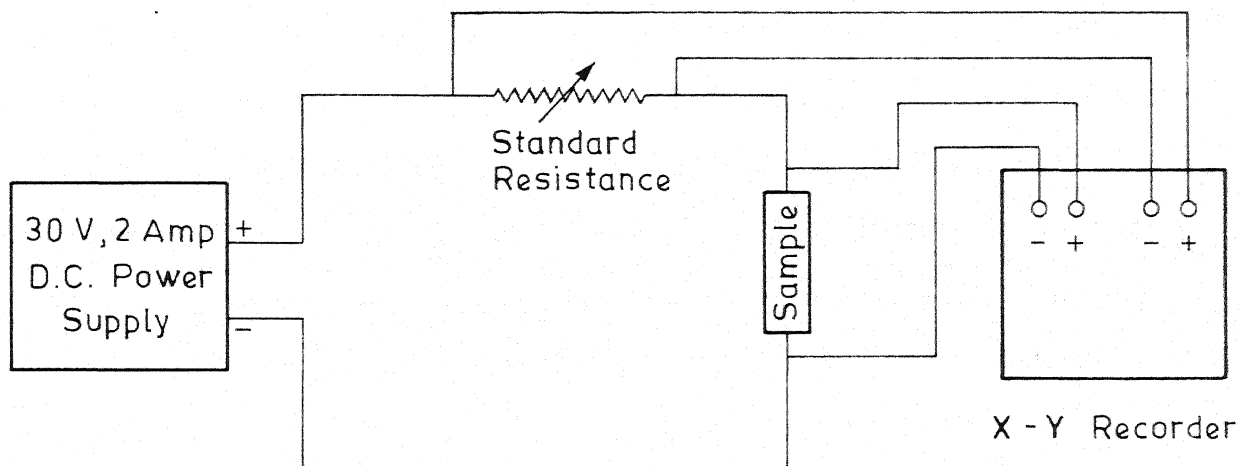


Fig. 3.2 Schematic representation of electrical circuit .



### 3.3.6.2 Measuring cell<sup>107</sup>

Figure 3.3 shows the schematic view of the cell used for electrical measurements. This consists of a double walled pyrex glass Jacket J, 300 mm long and having a diameter of 50 mm.  $E_1$  and  $E_2$  are two gold plated copper electrodes being placed co-axially with the metallic hollow cylinder S. They are separated from the metallic hollow cylinder S by two teflon discs T. The lower electrode  $E_1$  is fixed while the upper electrode  $E_2$  can move up and down. The electrodes are connected to the BNC connectors B with shielded wires. The sample can be placed between the two electrodes by inserting it through a rectangular hole O in S. On the other side, a copper constant thermocouple is inserted through a small hole H. The sample holder assembly is suspended with the help of three brass rods R brazed to the upper copper flange W, with a rubber gasket G in between, H.C. is a heating coil wound on a porcelain tube. This is connected to a 30 volts 2 amperes regulated DC power supply through a proportional temperature controller. The copper constant thermocouple TC serves the purpose of measuring temperature as well as sensing element for temperature control. By this set up the temperature can be varied from room temperature to about  $150^{\circ}\text{C}$  with an accuracy of temperature control  $\pm 1^{\circ}\text{C}$ . The inside of the assembly can be flushed with dry inert gas. To make the inside of the assembly moisture free silica gel dessicant D is used.

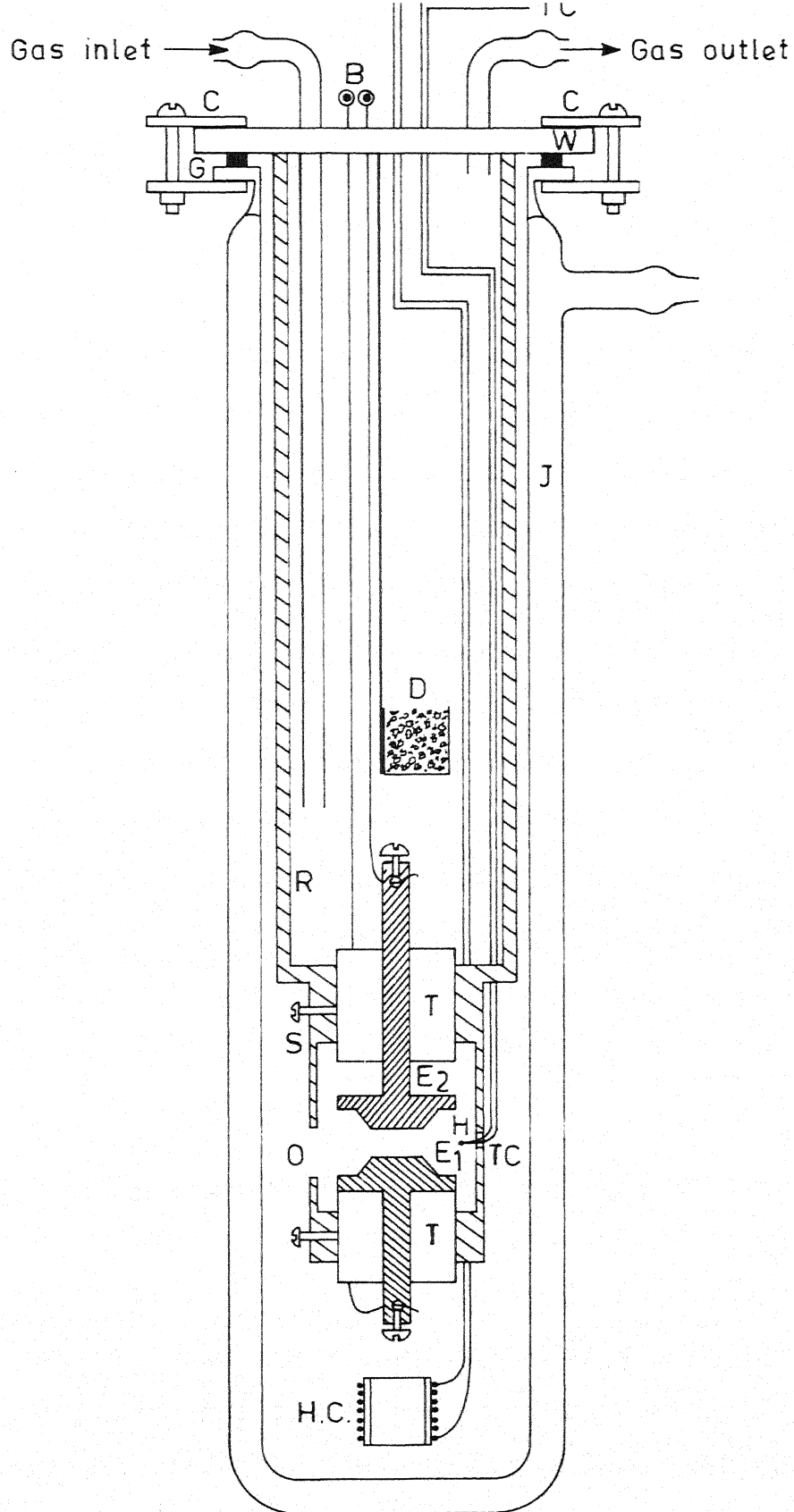


Fig. 3.3 Schematic diagram of the resistivity measuring cell .

### 3.4 Results and Discussion

#### 3.4.1 Switching characteristics of thin samples

Figures 3.4(a) and (b) show the theoretical I-V characteristics obtained for a film of thickness  $10\text{ }\mu\text{m}$  and electrode area  $6.3 \times 10^{-6}\text{ m}^2$  for different particle diameters and particle separation to diameter ratios. In figure 3.5 are shown the theoretical temperature distribution in a sample at different instants of time after the application of the critical field. It is seen that the time taken for the sample centre to attain the melting temperature of bismuth corresponding to a particle diameter  $700\text{ }\text{\AA}$  and separation to diameter ratio 0.03 is  $1.7 \times 10^{-4}$  second. In column 3 of table 3.1 we give the calculated time  $t_h$  for the entire sample to reach the melting temperature of bismuth for different values of  $d$  and  $s_0/d$  ratios. The kinetics of switching at room temperature is controlled by the heating step. However, we will show in Chapter 4 that the stretching kinetics is much faster.

In figure 3.6 the I-V characteristics obtained experimentally on a sample of identical geometry to that considered above are shown. It is noted that the sample switched to the memory state when potential drop across the sample is around 6.3 Volts. Also plotted in the figure are some theoretical I-V curves taken from figure 3.4(a) for particle diameter values of  $300\text{ }\text{\AA}$  and  $400\text{ }\text{\AA}$  and  $s_0/d$  ratios equal to 0.02 and 0.03. The agreement

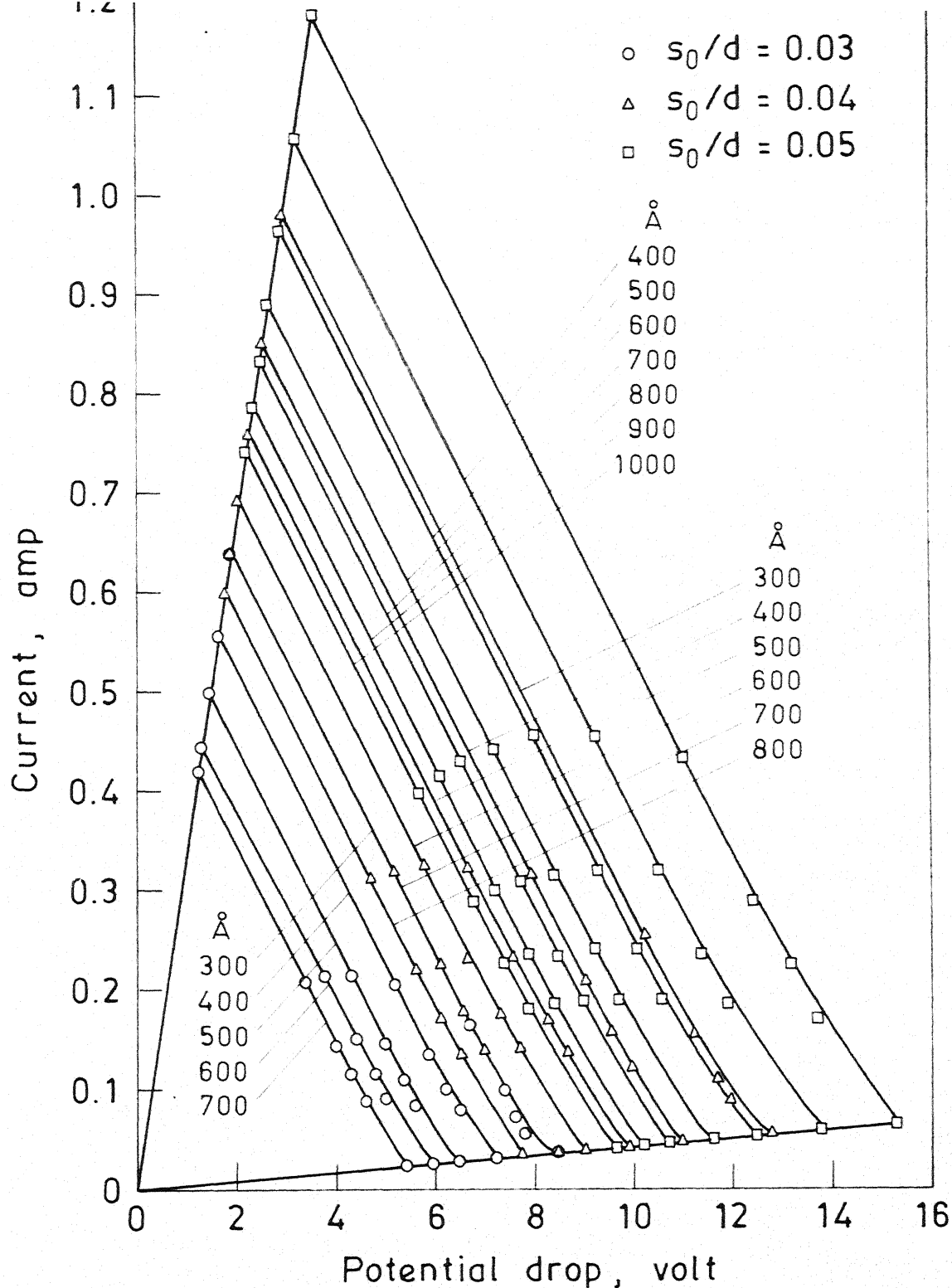


Fig. 3.4(a) Theoretical I-V characteristics for a glass-metal system of composition  $80\text{V}_2\text{O}_5$   $15\text{P}_2\text{O}_5$   $5\text{Bi}_2\text{O}_3$  (mole %) for various particle diameters  
 Sample thickness =  $10\text{ }\mu\text{m}$   
 Electrode area =  $6.3 \times 10^{-6}\text{ m}^2$

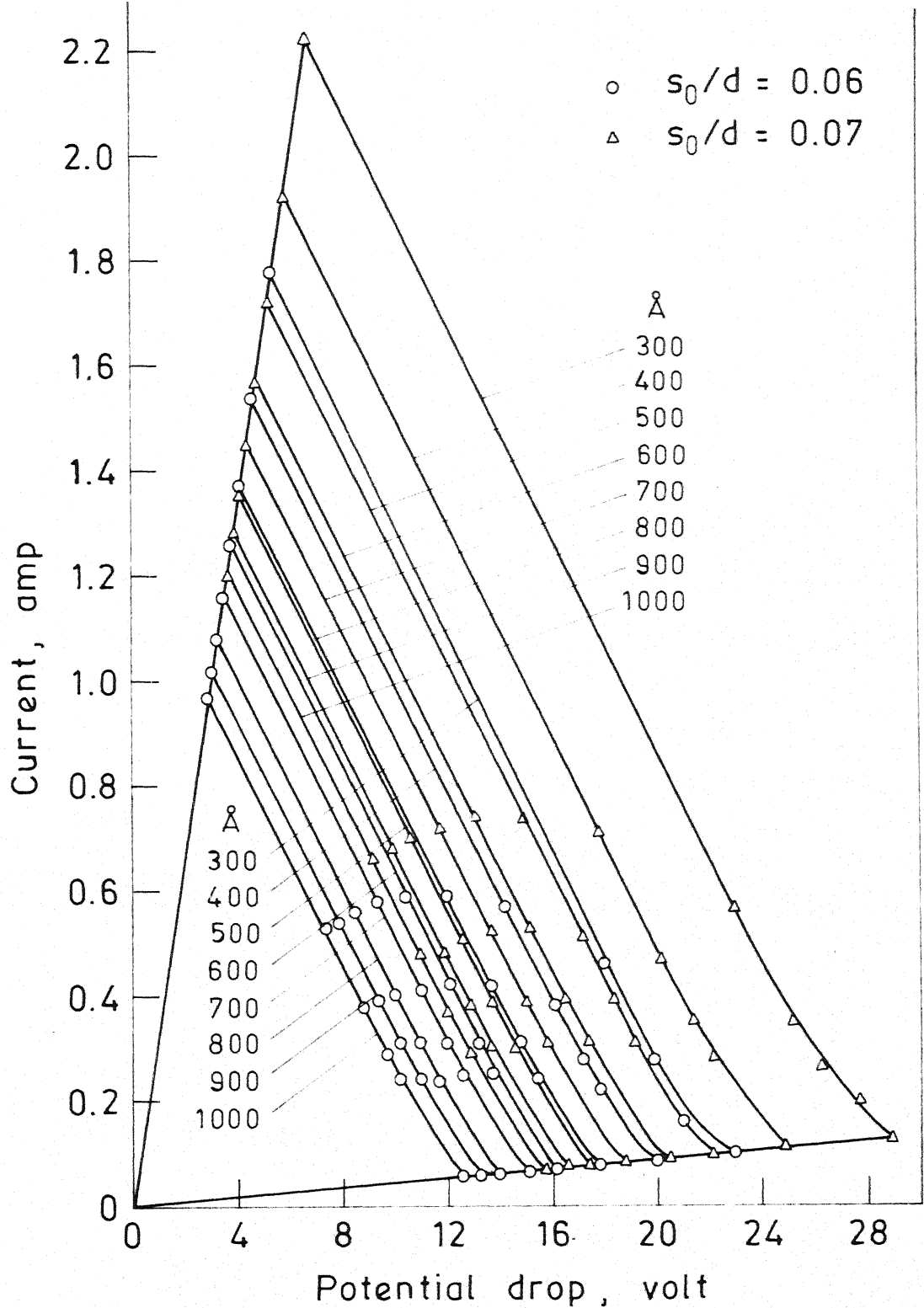


Fig. 3.4(b) Theoretical I-V characteristics of glass-metal system of composition  $80\text{V}_2\text{O}_5 15\text{P}_2\text{O}_5 5\text{Bi}_2\text{O}_3$  (mole %) for various particle diameters. Sample thickness =  $10\text{ }\mu\text{m}$ . Electrode area =  $6.3 \times 10^{-6}\text{ m}^2$

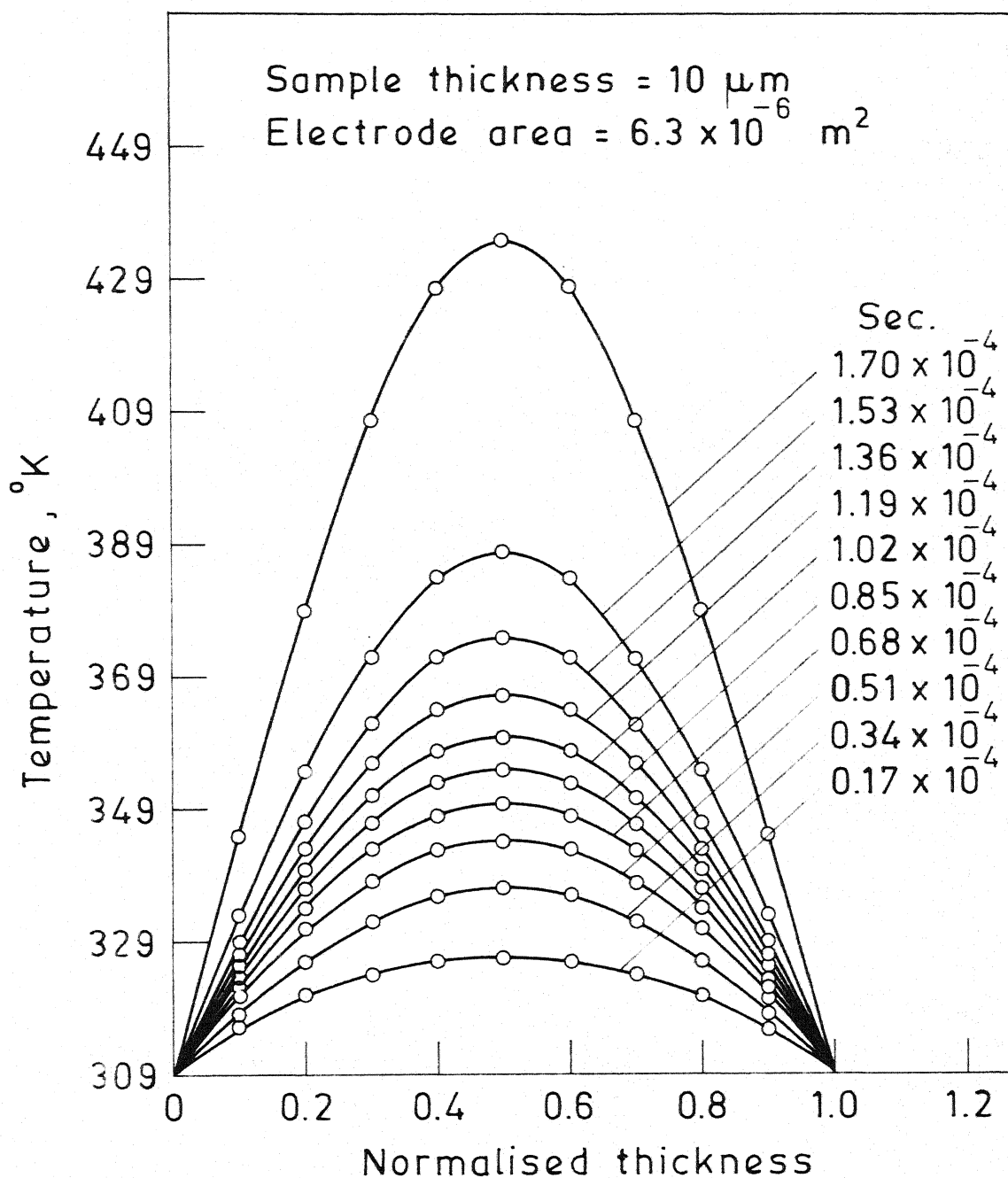


Fig. 3.5 Theoretical temperature profile within the glass-metal system of composition  $80\text{V}_2\text{O}_5$   $15\text{P}_2\text{O}_5$   $5\text{Bi}_2\text{O}_3$  (mole %) with  $d = 700\text{ }\text{\AA}$  and  $s_0/d = 0.03$ .

Table 3.1 Calculated parameters for switching in a glass of composition  $80V_2O_5, 15P_2O_5, 5Bi_2O_3$  (mole %) for different  $d$  and  $s_o/d$  values

Separation to diameter ratio $s_o/d$	Switching time $t_h$ controlled by heating step		Relaxation time $\tau$ for temperature profile	
	$\times 10^5$ $l=10\mu m$	sec. $l=45\mu m$	$\times 10^4$ $l=10\mu m$	sec. $l=45\mu m$
0.02	1.32	0.69	0.11	0.42
0.03	0.72	0.45	0.10	0.10
0.04	0.50	0.34	0.10	0.10
0.05	0.36	0.27	0.09	0.10
0.06	0.28	0.22	0.09	0.10
0.07	0.23	0.20	0.08	0.10
0.02	7.39	5.73	0.15	2.27
0.03	3.88	3.09	0.15	1.83
0.04	1.82	2.00	0.15	1.51
0.05	1.36	1.40	0.17	1.32
0.06	1.07	1.06	0.16	1.14
0.07	0.89	0.85	0.16	1.03
0.02	-	11.88	-	2.50
0.03	5.01	6.90	0.15	2.32
0.04	2.88	4.73	0.16	2.11
0.05	2.05	3.45	0.16	1.97
0.06	1.59	2.65	0.16	1.79
0.07	1.29	2.05	0.16	1.59

contd...

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600	0.02	-	21.72	-	2.55
	0.03	8.49	11.77	0.14	2.44
	0.04	4.15	8.20	0.14	2.35
	0.05	3.41	6.08	0.14	2.22
	0.06	2.12	4.76	0.15	2.11
	0.07	1.72	3.80	0.16	2.02
700	0.02	-	56.67	-	2.55
	0.03	18.46	19.50	0.14	2.50
	0.04	5.86	12.55	0.14	2.41
	0.05	3.69	9.20	0.14	2.32
	0.06	2.72	7.33	0.15	2.27
	0.07	2.16	5.91	0.16	2.19
800	0.02	-	-	-	-
	0.03	-	-	-	-
	0.04	8.60	19.10	-	2.47
	0.05	4.82	13.27	0.14	2.41
	0.06	3.42	10.25	0.14	2.35
	0.07	2.65	8.28	0.14	2.11
900	0.02	-	-	-	-
	0.03	-	-	-	-
	0.04	-	30.10	-	2.50
	0.05	6.36	18.88	0.14	2.44
	0.06	4.27	13.95	0.14	2.38
	0.07	3.23	11.10	0.14	2.35
1000	0.02	-	-	-	-
	0.03	-	-	-	-
	0.04	-	67.95	-	2.53
	0.05	8.63	29.11	0.14	2.50
	0.06	5.31	19.58	0.14	2.44
	0.07	3.90	14.90	0.14	2.41

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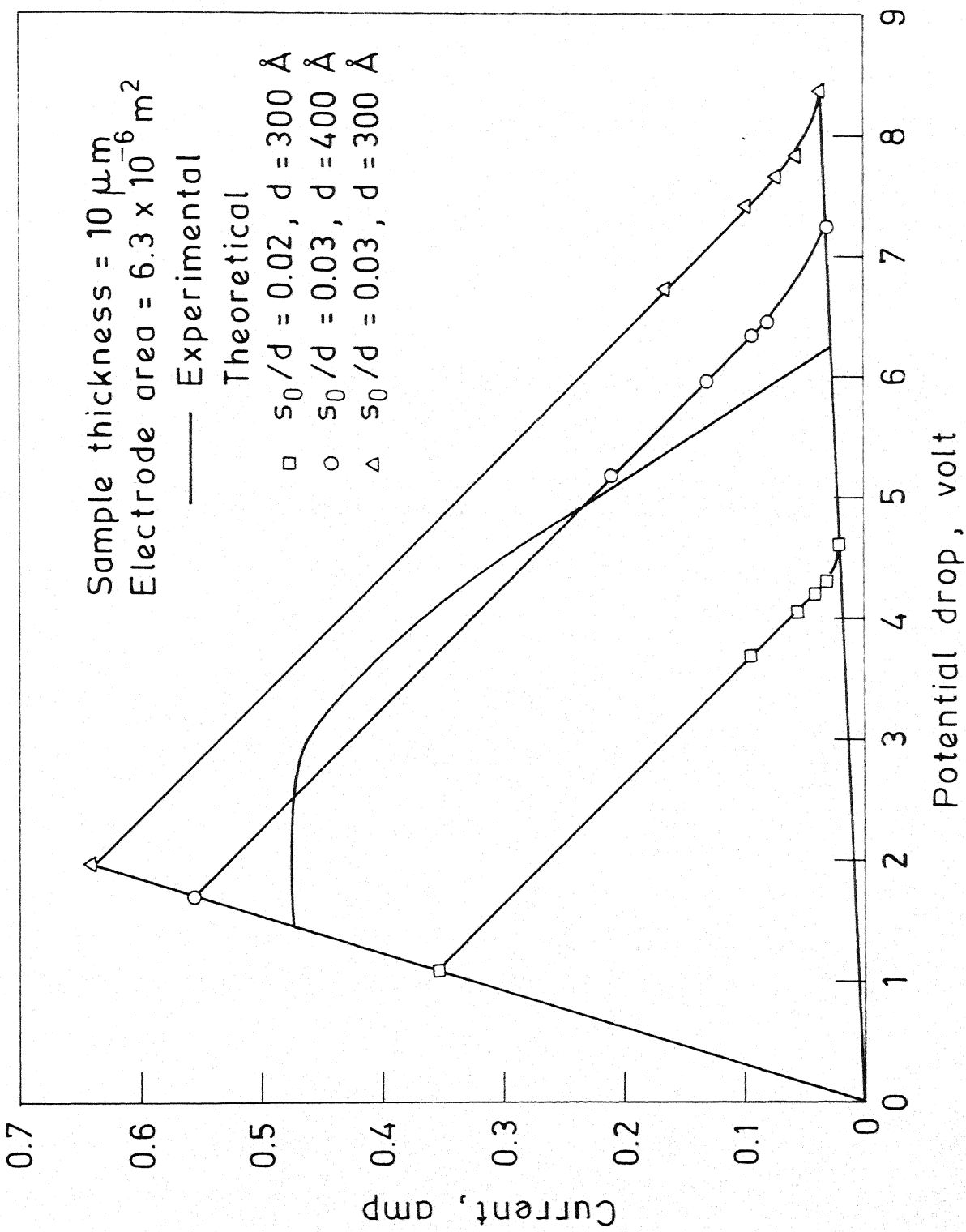


Fig. 3.6 Comparison of theoretical and experimental I-V curves.

between the two is found to be reasonable. Figures 3.7(a) and (b) give the electron micrograph and the selected area electron diffraction pattern of the sample respectively. The particles are observed to have diameters varying from 50 Å to 450 Å. In table 3.2 the interplanar spacings ( $d_{hkl}$ ) calculated from the diffraction pattern are compared with the standard values for bismuth<sup>108</sup> metal. The agreement between the two sets of values indicates that the particles comprise of metallic bismuth.

#### 3.4.2 Switching characteristics of thick samples

The effect of specimen thickness on the switching behaviour has been investigated by measuring the I-V characteristics of a sample of thickness 356 µm. No switching has been observed at room temperature and upto an applied voltage of 60 Volts. When the sample is however heattreated at 360°C for an hour it shows threshold switching with a threshold voltage of around 26 Volts.

Also the resistance of the heattreated sample is about an order of magnitude lower than that of the untreated one. The heattreatment is believed to cause further precipitation of metallic bismuth in the glass matrix thereby bringing about coalescence of larger particles which effectively gives rise to the formation of metallic region in a major portion of the glass-metal particulate system. This is substantiated as follows :

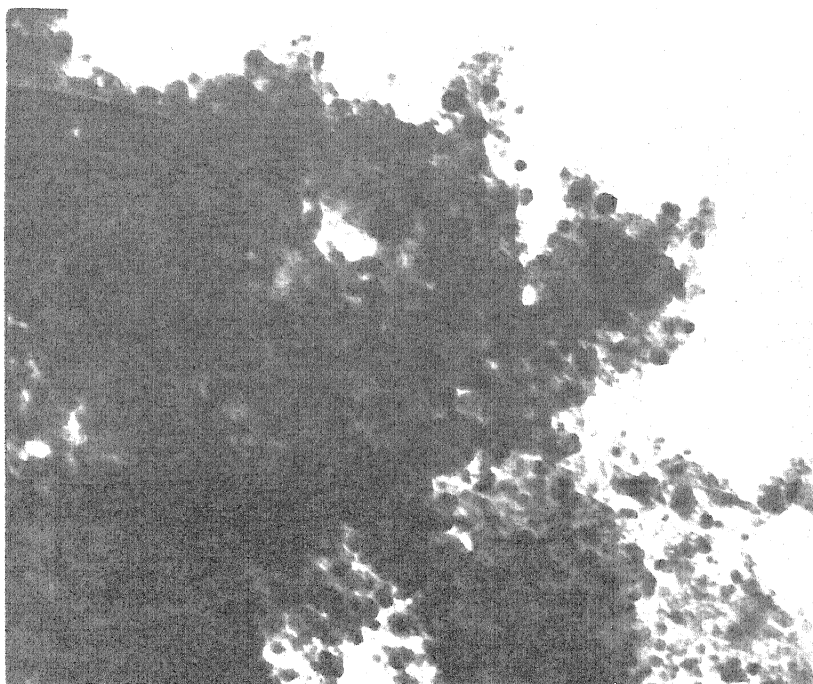


Fig.3.7(a) Electron micrograph of a sample  
of composition  $80\text{V}_2\text{O}_5, 15\text{P}_2\text{O}_5,$   
 $5\text{Bi}_2\text{O}_3$  (mole %)  
X 84,000

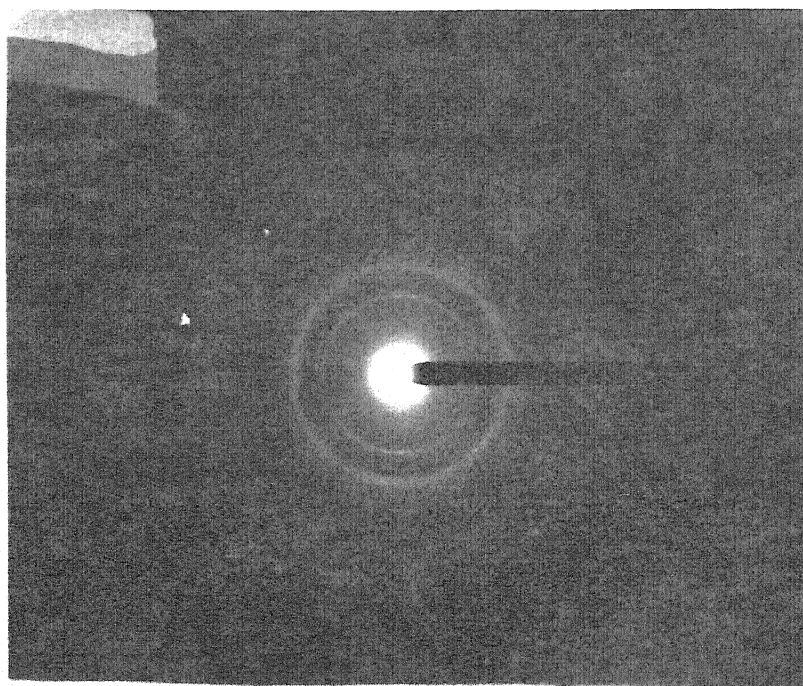


Fig.3.7(b) Electron diffraction pattern from  
the above microstructure

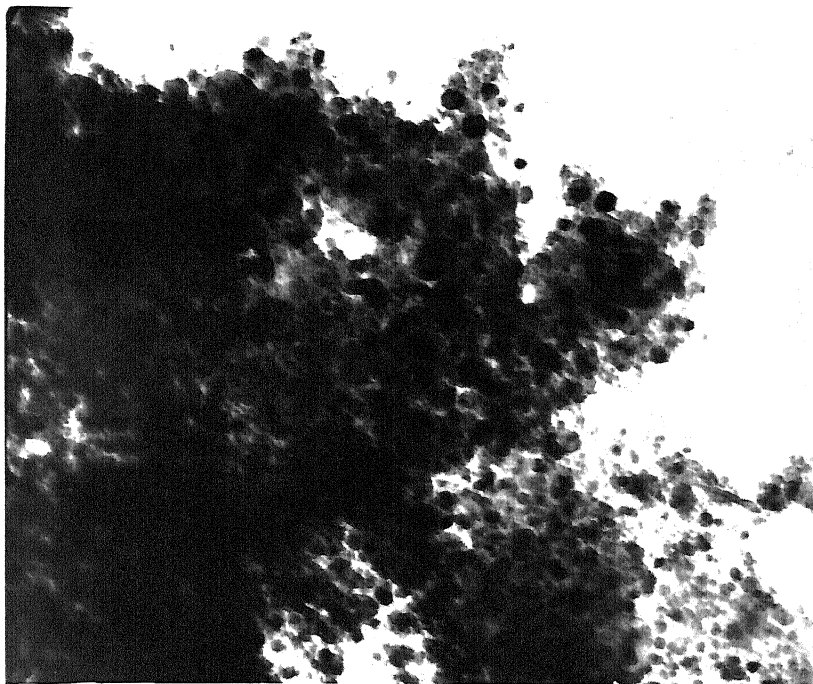


Fig.3.7(a) Electron micrograph of a sample  
of composition  $80\text{V}_2\text{O}_5$ ,  $15\text{P}_2\text{O}_5$ ,  
 $5\text{Bi}_2\text{O}_3$  (mole %)  
X 84,000

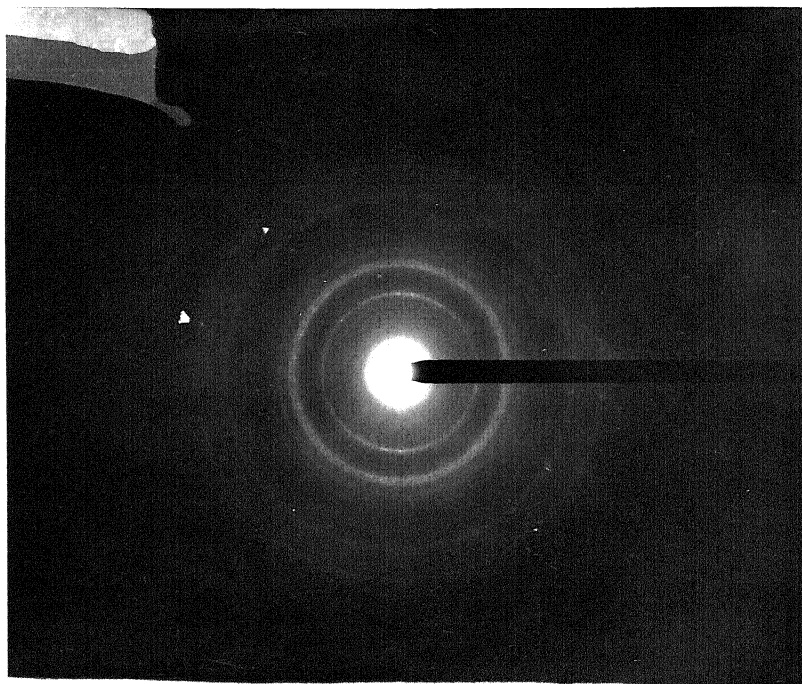


Fig.3.7(b) Electron diffraction pattern from  
the above microstructure

Table 3.2 Electron diffraction data for a  
glass-metal composite

$d_{hkl}$ values calculated from experimental data Å	Standard $d_{hkl}$ values of bismuth metal <sup>108</sup> Å
3.30	3.28
2.89	-
2.18	2.27
2.07	2.03
1.86	1.87
1.64	1.64
1.30	1.31
1.11	1.12

Figure 3.8 shows the DTA curve obtained for the as-cast glass. The exothermic peak at  $360^{\circ}\text{C}$  indicates that some crystalline phase is precipitated within the glass matrix at this temperature. In figure 3.9 are shown the X-ray diffraction patterns of the as-cast glass and of the sample heated at  $359^{\circ}\text{C}$  for an hour respectively in the range of  $2\theta$  values where the most intense peak of the heat-treated sample occurs. Figures 3.10(a) and (b) give the electron micrograph and the selected area diffraction pattern respectively of a heat-treated sample. Table 3.3 summarises the X-ray and electron diffraction data of the same. It is evident from this table that the precipitated phase consists of metallic bismuth. Also from figure 3.9, it is obvious that the amount of metallic bismuth present in the heat-treated sample is higher than that in the untreated sample. From figure 3.10(a) we conclude that the bismuth particles in this sample have diameters in the range  $50\text{\AA}$  to  $700\text{\AA}$ .

Figure 3.11 gives the theoretical I-V curves obtained for a sample of thickness  $45\text{ }\mu\text{m}$  and electrode area  $16 \times 10^{-6}\text{ m}^2$  for different particle diameters and separation to diameter ratios. The above thickness value has been chosen such that the experimental data match closely the theoretical results, for particle diameter values  $400\text{ }\text{\AA}$  and  $500\text{ }\text{\AA}$  and  $s_0/d$  value equals to 0.03, as shown in figure 3.12. From the discussion given above the effective thickness should be an order of magnitude smaller than

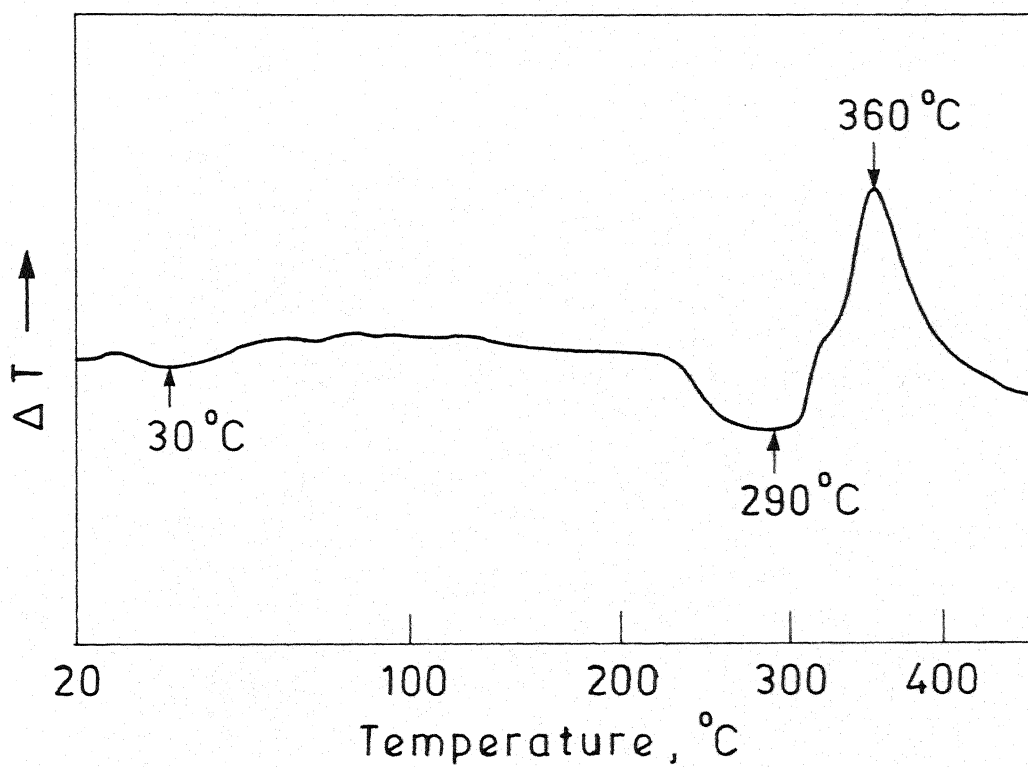


Fig. 3.8 DTA curve for a sample of composition  $80\text{V}_2\text{O}_5$   $15\text{P}_2\text{O}_5$   $5\text{Bi}_2\text{O}_3$  (mole %)

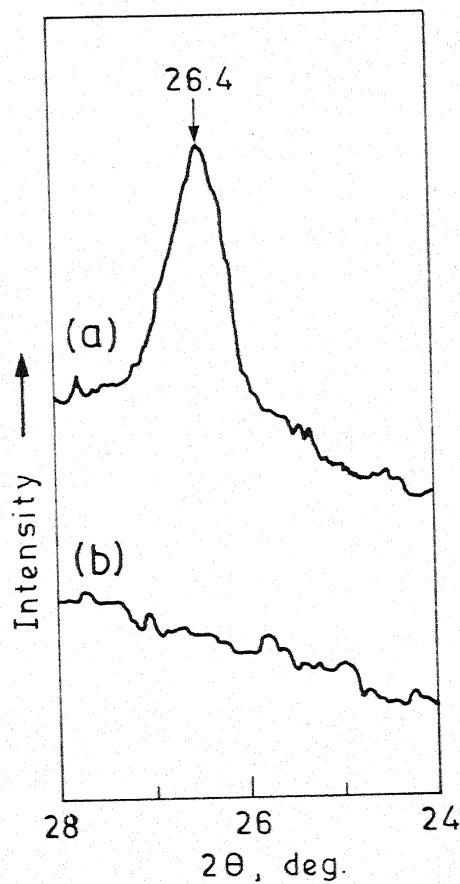


Fig. 3.9 X-ray diffraction pattern for a sample of composition 80V<sub>2</sub>O<sub>5</sub> 15P<sub>2</sub>O<sub>5</sub> 5Bi<sub>2</sub>O<sub>3</sub> (mole %)  
(a) Heat-treated at 359°C for 1 hour  
(b) As-cast.



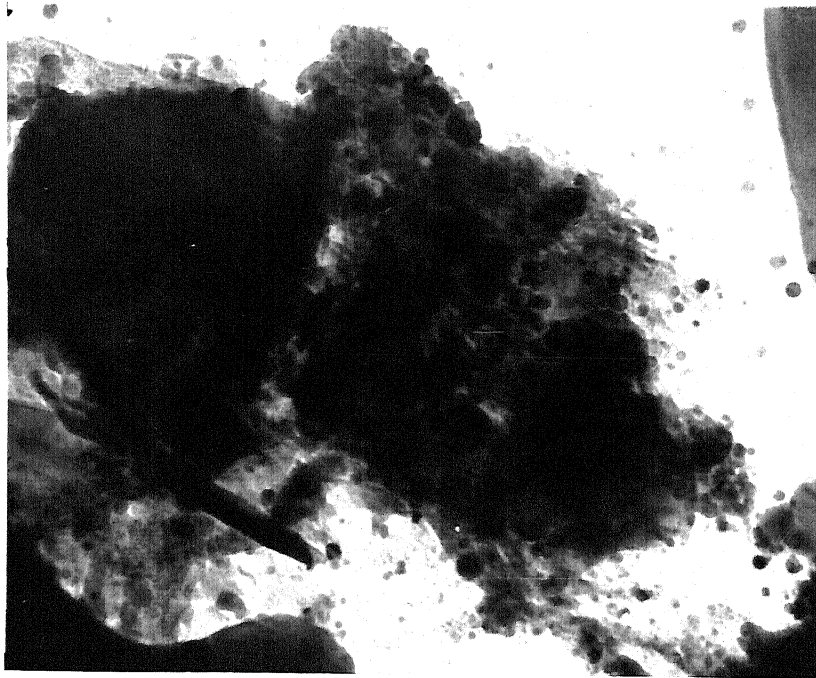


Fig.3.10(a) Electron micrograph of a sample of composition 80V<sub>2</sub>O<sub>5</sub>, 15P<sub>2</sub>O<sub>5</sub>, 5Bi<sub>2</sub>O<sub>3</sub> (mole %) after being heat-treated at 359°C for 1 hour  
X 84,000

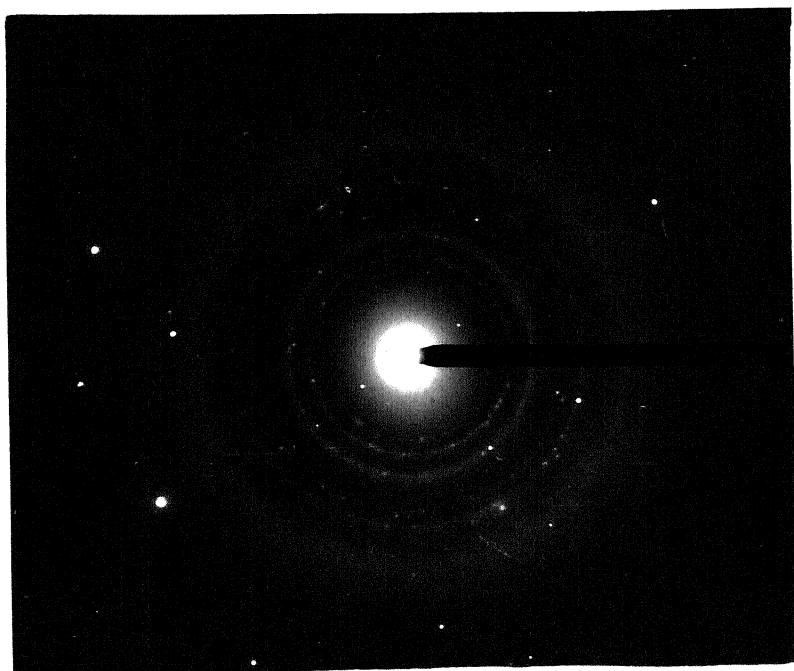


Fig.3.10(b) Electron diffraction pattern from the above microstructure

Table 3.3 X-ray and electron diffraction data for  
a glass-metal composite heated at 359°C  
for 1 hour

$d_{hkl}$ values calculated from electron diffraction	$d_{hkl}$ values calculated from X-ray diffraction	Standard $d_{hkl}$ values of bismuth metal <sup>108</sup>
Å	Å	Å
-	4.39	-
-	3.37	3.28
-	2.90	-
2.56	-	2.39
2.23	2.18	2.27
1.84	-	1.87
-	1.50	1.49
1.42	-	1.44
1.29	-	1.28

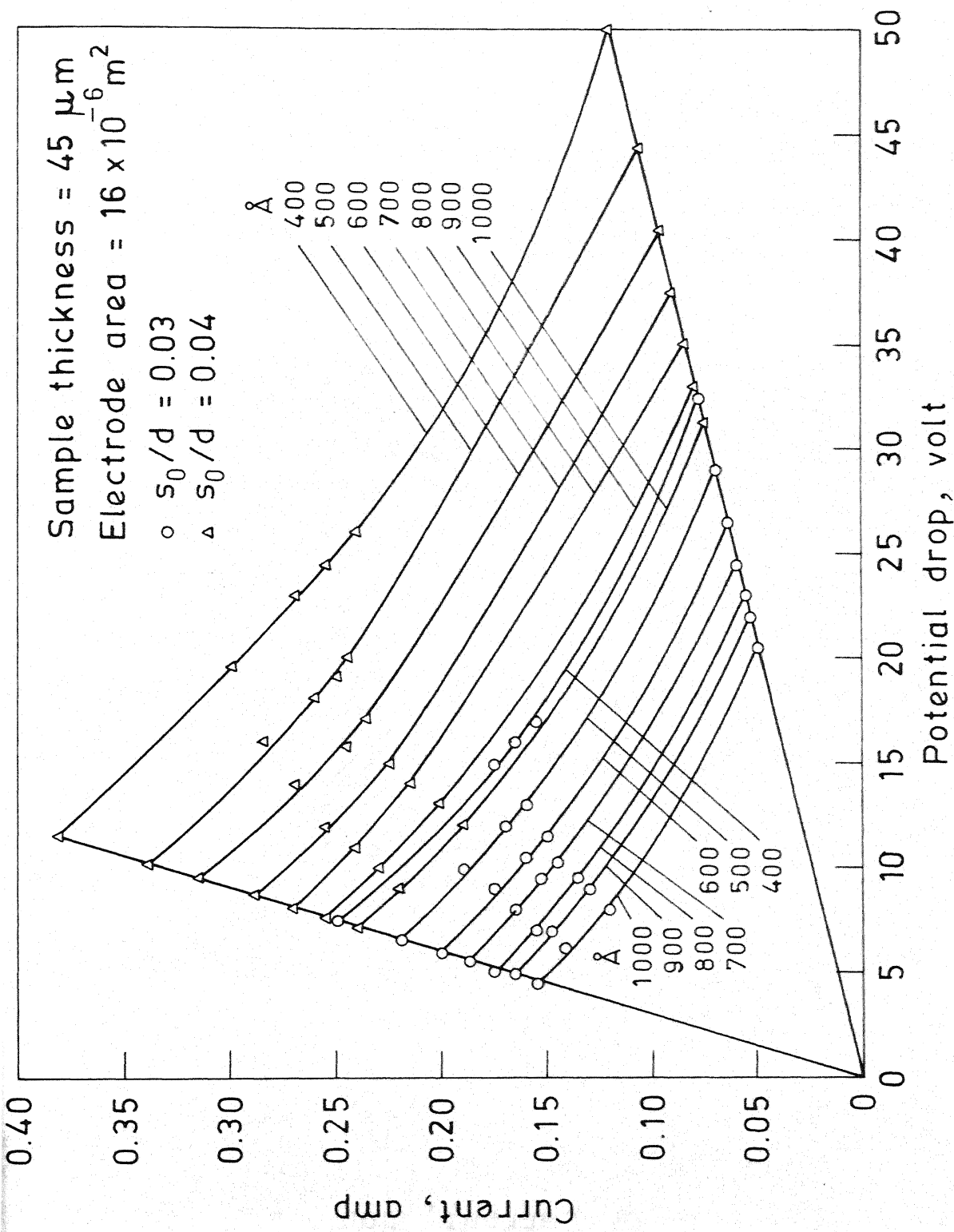


Fig. 3.11 (a) Theoretical I-V characteristics for a sample of composition  $80\text{V}_2\text{O}_5-15\text{P}_2\text{O}_5-5\text{Bi}_2\text{O}_3$  (mole %) for various particle diameters.

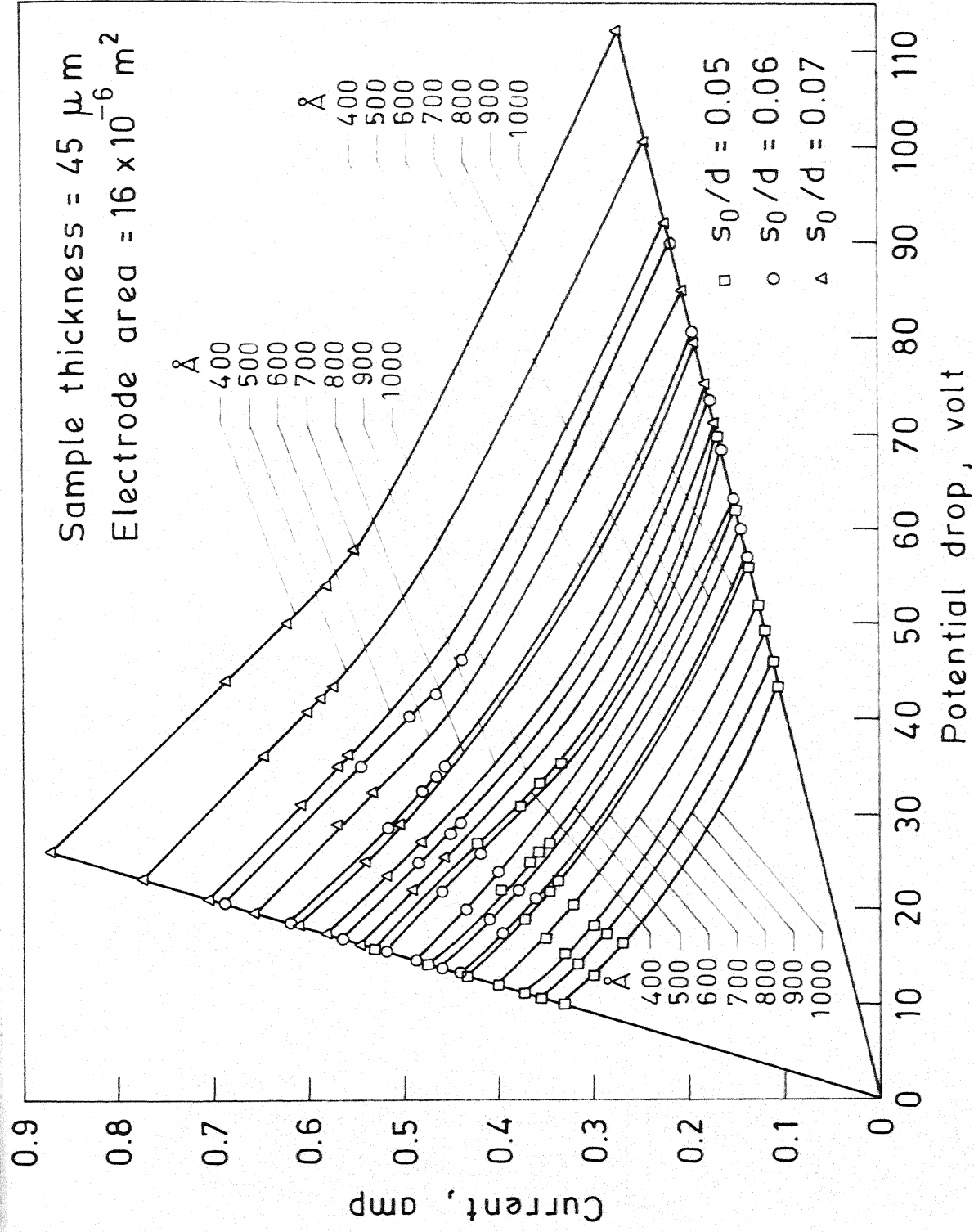


Fig. 3.11(b) Theoretical I-V characteristics for a sample of composition  $80\text{V}_2\text{O}_5 15\text{P}_2\text{O}_5 5\text{Bi}_2\text{O}_3$  (mole %) for various particle diameters.

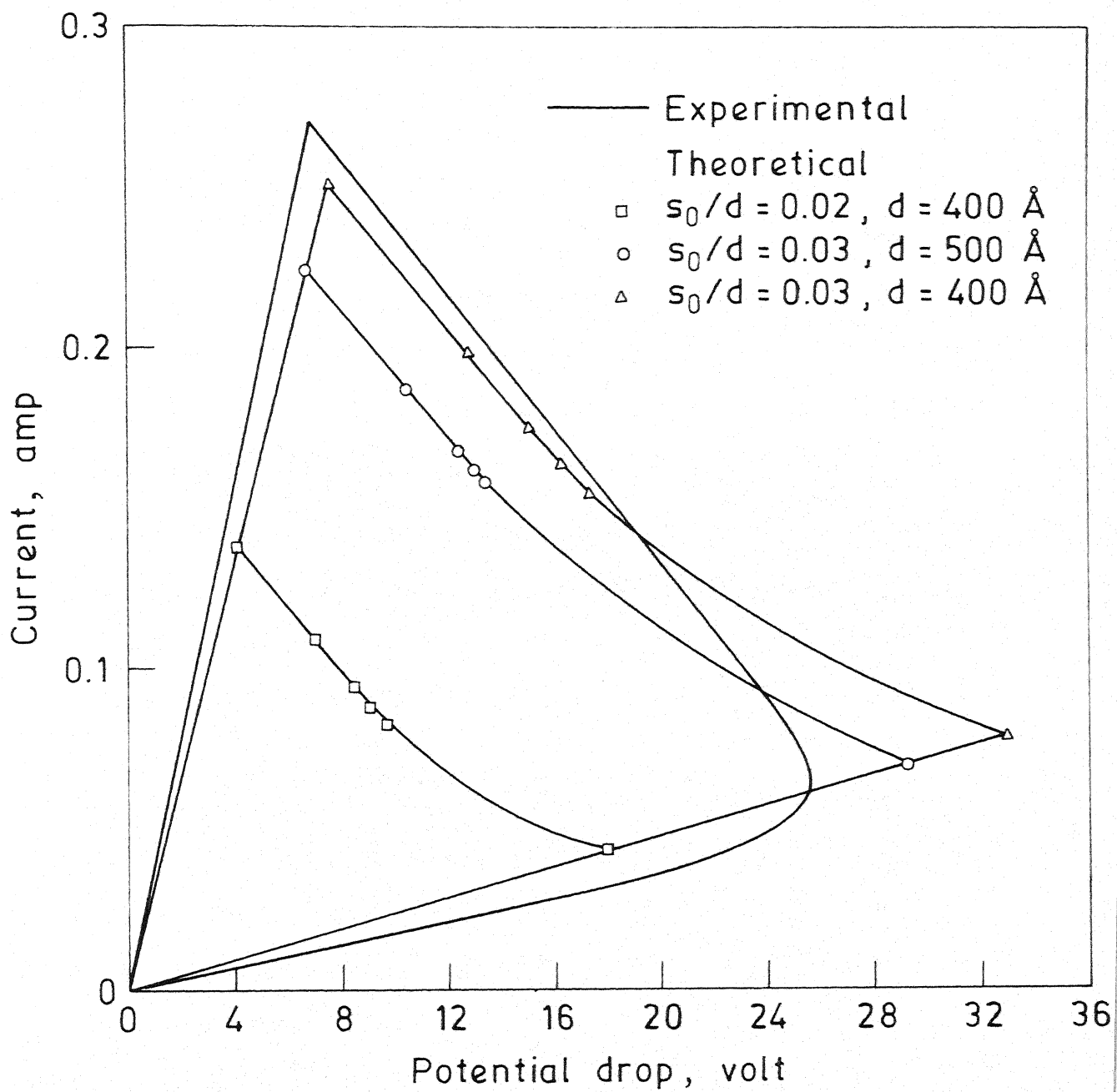


Fig. 3.12 Comparison of theoretical and experimental I-V curves .

Sample thickness =  $45 \mu\text{m}$   
 Electrode area =  $16 \times 10^{-6} \text{ m}^2$

the actual thickness ( $356\text{ }\mu\text{m}$  in our case). Our estimated value ( $45\text{ }\mu\text{m}$ ) therefore seems reasonable. In column 4 of table 3.1 we give the calculated time required for the entire sample to reach the melting temperature of bismuth for various  $d$  and  $s_0/d$  values. The time  $t_h$  for the thick sample is found to be in general greater than that for the thin sample which is expected from physical reasons.

In contrast to thin sample the threshold switching behaviour of thick sample can be explained from the calculated values of relaxation time  $\tau$  which has been defined earlier (Section 3.2.3) as the time required for the temperature at the centre of the sample to go below the melting temperature of bismuth after the applied electric field is reduced to zero. The relaxation time has been computed by the procedure outlined in Section 3.2.3 and Section 3.2.4.2 for different  $d$  and  $s_0/d$  values and for both the sample thicknesses under investigation. Figure 3.13 shows a typical calculated temperature profile as a function of time for a sample of thickness  $10\text{ }\mu\text{m}$  with  $d$  and  $s_0/d$  values of  $400\text{ }\text{\AA}$  and  $0.03$  respectively. The results are summarised in the last two columns of table 3.1. It is evident from these data that  $\tau$  values obtained for the sample with a thickness of  $45\text{ }\mu\text{m}$  are an order of magnitude higher than those of the thinner one ( $10\text{ }\mu\text{m}$ ). If the rate of removal of the electric field is faster as compared to the relaxation time  $\tau$ , it is likely that the stretched particles

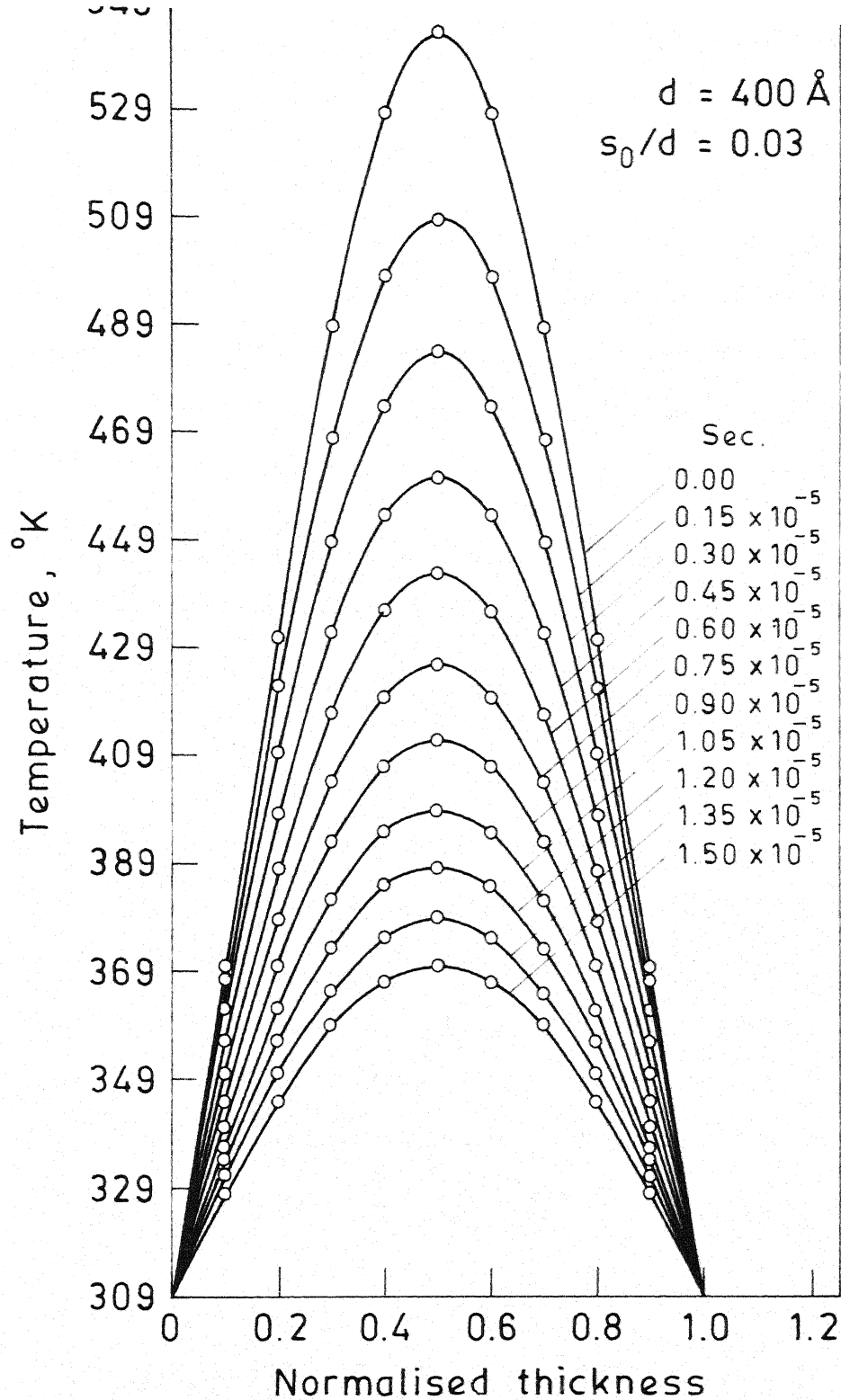


Fig. 3.13 Theoretical relaxation of temperature profile within a sample of composition  $80\text{V}_2\text{O}_5$   $15\text{P}_2\text{O}_5$   $5\text{Bi}_2\text{O}_3$  (mole %) after the removal of the electric field. Sample thickness =  $10 \mu\text{m}$ .

will regain their original shape due to the surface tension forces still effective in the molten state of metal granules. This will break the interconnections between the conducting particles and the sample will go back to the off-state. The occurrence of threshold switching in the case of the thick sample investigated here is therefore believed to arise due to a higher value of  $\tau$  pertaining to the specimen.

#### 3.4.3 Temperature dependent memory state resistance variation

Figure 3.14 shows a typical variation of resistance in the memory state of the blown thin film as a function of temperature over the range  $20^{\circ}\text{C}$  to  $110^{\circ}\text{C}$ . Before switching the off-state resistance of the sample is 1070 Ohms. It goes to the memory state via a negative resistance region at an applied voltage of 9.5V at  $23^{\circ}\text{C}$ . The resistance in the memory state is 8.0 Ohms at the same temperature. It is found from figure 3.14 that the on-state resistance remains constant with temperature. At  $107^{\circ}\text{C}$  the sample goes to the off-state of resistance about 8000 Ohms with an application of 0.5 volt. This behaviour can be explained as follows. According to particle stretching model, if the particles are in molten condition in the on-state, the removal of electric field causes the stretched particles to go back to their original shapes due to surface tension. Thus, the interconnections of the metallic chains are broken and a high resistance off-state is achieved. This condition is



realised by heating the sample in the memory state to  $107^{\circ}\text{C}$  along with an applied voltage of 0.5 Volt. It is believed that the role of the applied voltage is to help achieving the melting temperature of bismuth.

A similar behaviour has been reported in the case of silicate glass system containing bismuth at high temperature alone<sup>51</sup>.

When the interconnected chains in the memory state between the molten bismuth particles are broken due to the effect of surface tension force, the resistance of the sample increases and at the same time the increased resistance of the sample causes the current to decrease. Thus more the breaking of the interconnected chains the greater is the resistance of the sample and therefore the potential drop across the sample increases along with a reduction of current giving rise to a voltage controlled negative resistance region in the I-V characteristics. Figure 3.15 is the I-V plot of another sample in the on-state at  $78^{\circ}\text{C}$ . The sample goes to off-state at 0.18 Volt through a voltage controlled negative resistance region. Similar voltage controlled negative resistance region has been observed in the insulating thin film sandwiched between two metallic electrodes due to thermal rupture of conducting filaments<sup>109,110</sup>.

A number of samples has been studied which show qualitatively same behaviour as described above.

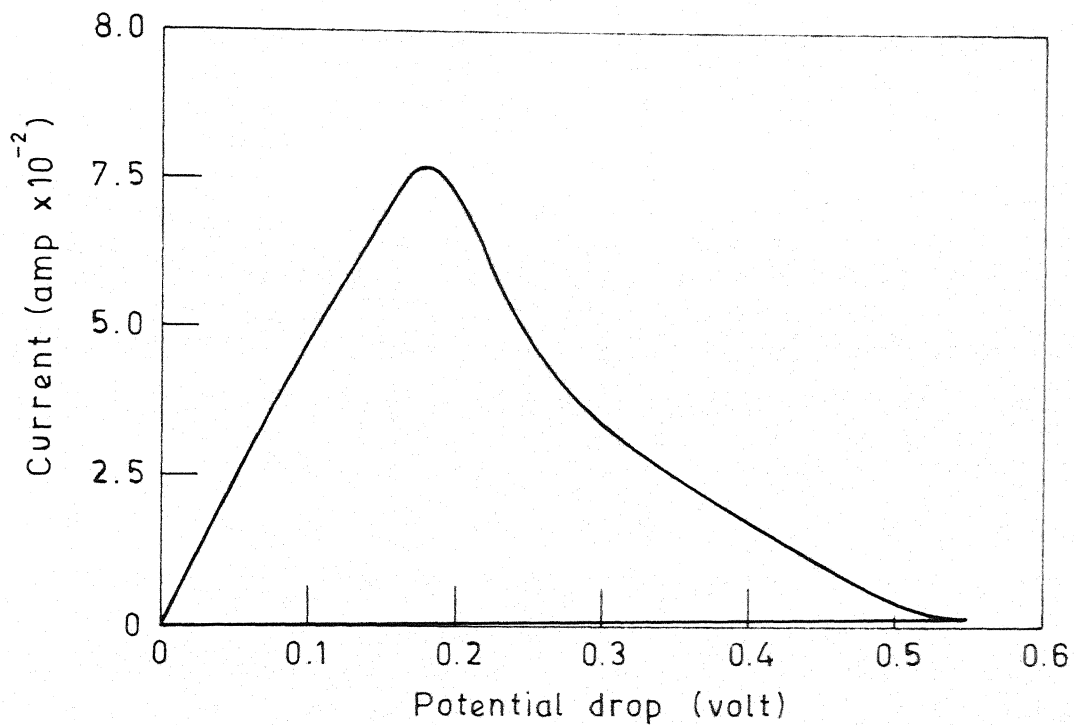


Fig. 3.15 I - V plot of 80V<sub>2</sub>O<sub>5</sub>-15P<sub>2</sub>O<sub>5</sub>-5Bi<sub>2</sub>O<sub>3</sub> (mole %) glass switching from on to the off-state at 78°C.

## CHAPTER 4

### KINETICS OF SWITCHING IN VANADIUM PHOSPHATE GLASSES CONTAINING BISMUTH GRANULES

#### 4.1 Introduction

In Chapter 2, we have developed a model. This predicts the critical switching fields which are of the same order as those obtained experimentally. In Chapter 3 with the help of the model developed in Chapter 2, the I-V characteristics especially in the negative resistance region have been computed. There it has been assumed that once the temperature reaches the size dependent melting point of bismuth interconnected chains are formed because of the presence of critical electric field. This implies that the time required for two physically proximate grains to touch each other in molten condition is much less compared to the time required for the temperature profile to reach the melting temperature of bismuth. In this chapter, we present the solution for the dynamics of stretching and compute the time required for two physically proximate grains to touch each other in molten condition after the application of critical switching field.

#### 4.2 Theoretical Consideration

When an electric field is applied to a glass-metal composite, the metallic particles in the molten state will be

stretched as described in Chapter 2. Figure 2.3 of Chapter 2 shows, at some instant of time, the state of two proximate grains during stretching into ellipsoidal forms from spherical shapes. The problem is to find the time required by each sphere to elongate by a distance  $s_0/2$ , so that the particles can join up. It is noted that the boundary of the ellipsoid changes during stretching. This moving boundary fluid flow problem has been analysed with the help of well known fluid flow equations.

The following assumptions have been made in our analysis for simplicity of calculations.

- 1) The molten liquid is inviscid i.e., the viscous drag has been neglected compared to surface tension.
- 2) The flow is irrotational and the liquid is incompressible.
- 3) The flow problem has been solved in two dimensions.

#### 4.2.1 Determination of potential $\phi_f$

To determine the force acting on the deformed granule at a distance  $x$  from the origin, we use the same method as described in Section 2.2.1 of Chapter 2. By displacing the ellipsoid by  $\delta x$  (figure 4.1) against the force  $F_{el}|_x$  in the negative direction of  $x$ , we can write,

$$F_{el}|_x \delta x = \frac{1}{2} \epsilon \epsilon_0 E^2 \delta V \quad (4.1)$$

where  $\delta V$ , is the volume as cross-hatched in figure 4.1.

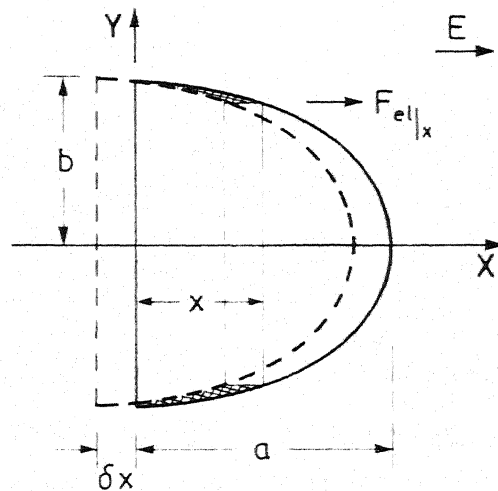


Fig. 4.1 Configuration of a half ellipsoid stretched under the action of an electric field .

Its value is obtained by integrating the equation (2.4) of Chapter 2 from  $x = 0$  to  $x = x$  and we get,

$$\delta V = \pi \left( \frac{b^2}{a^2} \right) x^2 \delta x \quad (4.2)$$

where  $a$  and  $b$  are semi-major and semi-minor axes of the ellipse respectively.

Substituting equation (4.2) into equation (4.1) and after simplification, we get,

$$F_{el} \Big|_x = \frac{1}{2} \pi \epsilon \epsilon_0 E^2 \left( \frac{b^2}{a^2} \right) x^2 \quad (4.3)$$

This force will act on the mass of the ellipsoid between  $x = 0$  and  $x = x$ . The volume ( $V$ ) of ellipsoid between  $x = 0$  and  $x = x$  is given by,

$$V = \int_0^x \pi y^2 dx \quad (4.4)$$

Writing  $y$  in terms of  $x$  from the equation of the ellipse and integrating we get,

$$V = \pi b^2 \left( x - \frac{x^3}{3a^2} \right) \quad (4.5)$$

The force per unit mass is therefore given by,

$$F = \frac{3}{2} \frac{\epsilon \epsilon_0 E^2}{\rho} \left( \frac{x}{3a^2 - x^2} \right) \quad (4.6)$$

where  $\rho$  is the density of the liquid.

In a conservative system, force  $\vec{F}$  is given by the expression,

$$\vec{F} = -\vec{\nabla}\varphi_f \quad (4.7)$$

where  $\varphi_f$  is the scalar potential.  $\varphi_f$  is obtained by integrating equation (4.7) and is given by,

$$\varphi_f = - \int_0^x F \, dx \quad (4.8)$$

Substituting  $F$  from equation (4.6) in equation (4.8) and integrating we get,

$$\varphi_f = - \frac{3}{4} \frac{\epsilon\epsilon_0 E^2}{\rho} \ln \left[ \frac{3a^2}{3a^2 - x^2} \right] \quad (4.9)$$

#### 4.2.2 Determination of pressure

The effective pressure  $\Delta P$  which is operative in restraining the fluid flow, is given by,

$$\Delta P = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) - \frac{2\gamma}{r} \quad (4.10)$$

where  $R_1, R_2$  are the radii of curvature of the ellipsoid and are given by the expressions (2.8) and (2.9) of Chapter 2.

$\gamma$  and  $r$  are the surface tension and radius of metallic particle.

Substituting  $y'$  and  $y''$  ( $y' = \frac{dy}{dx}$  and  $y'' = \frac{d^2y}{dx^2}$ ) in equation (4.10) and on simplification we get,

$$\Delta P = \gamma \left[ \left( \frac{a}{b} \right) \left( \frac{1}{b} \right) \left\{ \frac{\left[ \left( \frac{a}{b} \right)^2 (1 - (x/a)^2) + 1 + (x/a)^2 \right]}{\left[ \left( \frac{a}{b} \right)^2 (1 - (x/a)^2) + (x/a)^2 \right]^{3/2}} \right\} - \frac{2}{r} \right] \quad (4.11)$$

### 4.2.3 Fluid flow equations

For an incompressible liquid the continuity equation is given by,

$$\vec{\nabla} \cdot \vec{q} = 0 \quad (4.12)$$

where  $q$  is the velocity vector and is given by,

$$\vec{q} = \vec{i} u + \vec{j} v \quad (4.13)$$

where  $u$  and  $v$  are the components of velocity in  $x$  and  $y$  directions respectively.

From the definition of circulation and Stokes theorem<sup>111</sup>,

$$\oint_c \vec{q} \cdot d\vec{r} = \iint_A \vec{n} \cdot (\vec{\nabla} \times \vec{q}) \quad (4.14)$$

where  $\oint_c$  indicates the integration over a closed contour  $c$  in the liquid and  $A$  the area enclosed by this contour. Since the liquid flow is irrotational,

$$\vec{\nabla} \times \vec{q} = 0 \quad (4.15)$$

Hence from equation (4.14) we get,

$$\oint_c \vec{q} \cdot d\vec{r} = 0 \quad (4.16)$$

Equation (4.16) implies<sup>98</sup> that,

$$\vec{q} = \vec{\nabla} \phi \quad (4.17)$$



where  $\varphi$  is a single valued scalar velocity potential function. Substituting equation (4.17) in (4.12), the continuity equation becomes,

$$\nabla^2 \varphi = 0 \quad (4.18)$$

For an inviscid liquid, the Navier-Stokes equation is given by<sup>111</sup>,

$$\frac{D\vec{q}}{Dt} = \frac{\partial \vec{q}}{\partial t} + (\vec{q} \cdot \nabla) \vec{q} = \vec{F} - \frac{\nabla P}{\rho} \quad (4.19)$$

where  $\vec{F}$  is the body force per unit mass,  $\nabla P$  the pressure gradient and  $\rho$  the density of liquid.

In a conservative system, the body force is given by equation (4.7). Substituting equation (4.7) in (4.19),

$$\frac{D\vec{q}}{Dt} = - \nabla \varphi_f - \frac{\nabla P}{\rho} \quad (4.20)$$

For irrotational flow<sup>111</sup> the  $(D\vec{q}/Dt)$  can also be written as,

$$\frac{D\vec{q}}{Dt} = \nabla \left( \frac{\partial \varphi}{\partial t} + \frac{1}{2} \nabla \cdot \vec{q}^2 \right) \quad (4.21)$$

The integration in equation (4.16) is evaluated at a fixed time. Hence, the time derivative can be written as,

$$\oint_C \frac{D}{Dt} (\vec{q} \cdot d\vec{r}) = 0 \quad (4.22)$$

or

$$\oint_C \left( \frac{D\vec{q}}{Dt} \cdot d\vec{r} + \vec{q} \cdot d\vec{q} \right) = 0 \quad (4.23)$$

Substituting  $\frac{D\vec{q}}{Dt}$  from equation (4.20) in equation (4.23) and integrating we get,

$$-\varphi_f - \frac{P}{\rho} + \frac{1}{2} q^2 = 0 \quad (4.24)$$

Similarly substituting  $\frac{D\vec{q}}{Dt}$  from equation (4.21) in equation (4.23) and integrating we get,

$$\frac{\partial \varphi}{\partial t} + q^2 = 0 \quad (4.25)$$

Equating (4.24) and (4.25) we get,

$$\frac{\partial \varphi}{\partial t} = -(\varphi_f + \frac{P}{\rho} + \frac{1}{2} q^2) \quad (4.26)$$

Substituting  $\varphi_f$  and  $P$  from equations (4.9) and (4.11) respectively and putting the dot product of  $\vec{q}$  (equation 4.13) in equation (4.26) we get,

$$\frac{\partial \varphi}{\partial t} = \frac{3}{4} \frac{\epsilon \epsilon_0 E^2}{\rho} \ln \frac{3a^2}{3a^2 - x^2} - \frac{1}{2}(u^2 + v^2) - \frac{\gamma}{\rho} \left[ \left( \frac{a}{b} \right) \left( \frac{1}{b} \right) \left\{ \frac{(a/b)^2(1-x^2/a^2) + (1+x^2/a^2)}{[(a/b)^2(1-x^2/a^2) + (x^2/a^2)]^{3/2}} \right\} - \frac{2}{r} \right] \quad (4.27)$$

In our analysis the closed contour is the boundary of the liquid droplet. From symmetry of the geometrical shape we consider only the first quadrant in the  $x$ - $y$  plane. viz.,  $0 \leq x \leq a$  and  $0 \leq y \leq b$ .

As we have mentioned earlier, the boundary moves with time. Therefore, one has to consider the dynamic boundary condition. This is given by<sup>112</sup>,

$$\left. \frac{\partial V}{\partial t} \right|_{\text{boundary}} = [v - u \frac{\partial V}{\partial x}] \Big|_{\text{boundary}} \quad (4.28)$$

Initial conditions, at  $t = 0$ , are

$$u = v = \varphi = \frac{\partial \varphi}{\partial t} = 0 \quad (4.29)$$

According to our assumption, the initial shape is spherical.

At  $t > 0$ , from symmetry consideration, along the straight boundaries ( $x = 0$ ,  $y = 0$ ),  $\frac{\partial \varphi}{\partial x} = 0$  and  $\frac{\partial \varphi}{\partial y} = 0$  respectively. Along the curved boundary, the functional value of  $\varphi$  is obtained from the solution of the equation (4.27). Thus, the problem is to solve the Laplace equation (4.18) consistent with the above boundary conditions. Since no analytical solution is available, we have solved the equation numerically by using a finite difference scheme.

### 4.3 Numerical Solution

For ease of computation it is necessary to normalise the equations. The normalisation is carried out by setting,

$$X = x/a \quad (4.30)$$

$$Y = y/b \quad (4.31)$$

and

$$t^* = t/t_1 \quad (4.32)$$

such that

$$0 \leq X \leq 1, \quad 0 \leq Y \leq 1 \quad \text{and} \quad 0 \leq t^* \leq 1 \quad (4.33)$$

By using expressions (4.30) and (4.31) the Laplace equation (4.18) becomes,

$$\frac{1}{(a/b)^2} \frac{\partial^2 \phi}{\partial X^2} + \frac{\partial^2 \phi}{\partial Y^2} = 0 \quad (4.34)$$

By using expressions (4.30) to (4.32) equation (4.27) becomes,

$$\begin{aligned} \frac{1}{t_1} \frac{\partial \phi}{\partial t^*} &= \frac{3}{4} \frac{\epsilon \epsilon_0 E^2}{\rho} \ln \left( \frac{3}{3-X^2} \right) - \frac{1}{2} (u^2 + v^2) - \\ &\frac{\gamma}{\rho} \left[ \left( \frac{a}{b} \right) \left( \frac{1}{b} \right) \left\{ \frac{[(\frac{a}{b})^2 (1-X^2) + (1+X^2)]}{[(\frac{a}{b})^2 (1-X^2) + X^2]^{3/2}} \right\} - \frac{2}{r} \right] \end{aligned} \quad (4.35)$$

where,  $u$  and  $v$  after normalisation become

$$u = \frac{1}{a} \frac{\partial \phi}{\partial X} \quad (4.36)$$

$$v = \frac{1}{b} \frac{\partial \phi}{\partial Y} \quad (4.37)$$

Using equations (4.30) and (4.31), the equation (4.28) becomes,

$$b \frac{\partial Y}{\partial t} + \frac{\partial b}{\partial t} Y = v - u \frac{b}{a} \frac{\partial Y}{\partial X} \quad (4.38)$$

Substituting expressions (4.30) and (4.31) in an equation of ellipse, we get,

$$X^2 + Y^2 = 1 \quad (4.39)$$

Under this condition we must have,

$$\frac{\partial Y}{\partial t} = 0 \text{ and evaluating } \frac{\partial Y}{\partial X} \text{ from (4.39), the equation (4.38)}$$

becomes,

$$\sqrt{1-X^2} \frac{\partial b}{\partial t} = v + u \frac{b}{a} \frac{X}{\sqrt{1-X^2}} \quad (4.40)$$

The above equation is valid for any value of  $0 \leq X \leq 1$ . Therefore, at  $X = 0$  and using equation (4.32) equation (4.40) becomes

$$\frac{1}{t_1} \frac{\partial b}{\partial t^*} = v|_{X=0} \quad (4.41)$$

Since  $v$  is a function of time and its functional form is not known it has been evaluated numerically.

#### 4.3.1 Numerical scheme

Figure 4.2 represents the first quadrant in the X-Y plane in which the equations have been solved numerically. The normalised X and Y axes have been divided into 10 equal parts such that the steplengths are  $h = 0.1$  and  $k = 0.1$  respectively.  $X_0, X_{0.1}, \dots, X_{0.9}$  represent the points of intersection of the curve and the lines  $X = 0, X = 0.1, \dots, X = 0.9$ . Similarly  $Y_0, Y_{0.1}, \dots, Y_{0.9}$  represent the points of intersection of the curve and the lines  $Y = 0, Y = 0.1, \dots, Y = 0.9$ . These are the boundary points on the curve at which  $\phi$ 's have to be evaluated at a particular time so that the Laplace equation can be solved at that instant of time at the grid points as shown in figure 4.2. It is to be noted that the grid points marked with open circles near the boundary have unequal steplengths. The following steps are involved in the numerical solution of the problem<sup>112</sup>.

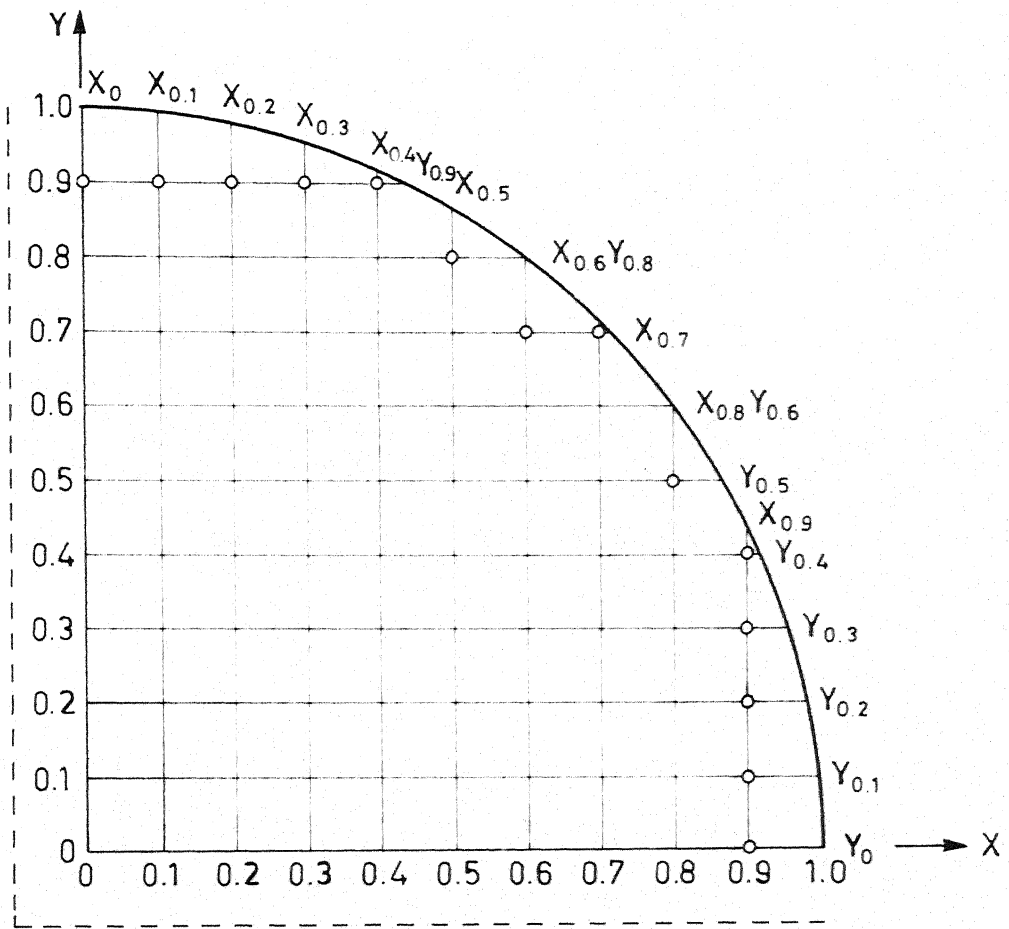


Fig. 4.2 Grid points in the first quadrant of a circle for solution of fluid flow equations.

- Step 1 :  $t_1$  is assigned an arbitrary value and the normalised time is divided into 10 parts such that step length  $p = 0.1$ ,  $t^* = 0$  is set.
- Step 2 : The first order partial derivative (of equation(4.35)) is replaced by backward difference. The finite difference formula becomes

$$\varphi_{t^*+p} = \varphi_{t^*} + t_1 p \left[ \frac{3}{4} \frac{\epsilon \epsilon_0 E_{t^*}^2}{\rho} \ln \left( \frac{3}{3-X^2} \right) - \frac{1}{2} (u_{t^*}^2 + v_{t^*}^2) - \frac{\gamma}{\rho} \left[ \left( \frac{a_{t^*}}{b_{t^*}} \right) \left( \frac{1}{b_{t^*}} \right) \left\{ \frac{(a_{t^*}/b_{t^*})^2 (1-X^2) + (1+X^2)}{\{(a_{t^*}/b_{t^*})^2 (1-X^2) + X^2\}^{3/2}} \right\} - \frac{2}{r} \right] \right] \quad (4.42)$$

$\varphi_{t^*+p}$  is evaluated from above equation at the boundary points,  $X_0, X_{0.1}, \dots, X_{0.9}, Y_0, Y_{0.1}, \dots, Y_{0.9}$ .  $E_{t^*}$  is given by the expression (2.18) of Chapter 2.

- Step 3 : At every grid point  $(i,j)$  the Laplace equation (4.34) is replaced by the following finite difference formula,

$$\frac{\varphi_{i-1,j} - 2\varphi_{i,j} + \varphi_{i+1,j}}{(a_{t^*}/b_{t^*})^2 h^2} + \frac{\varphi_{i,j-1} - 2\varphi_{i,j} + \varphi_{i,j+1}}{k^2} = 0 \quad (4.43)$$

Two things to be noted in the above formula.

First, for any  $j$ , when  $i = 0$ , we get  $\varphi_{-1,j}$ ,  $\varphi_{0,j}$  and  $\varphi_{1,j}$  in the first term of equation (4.43). From the boundary condition at  $t^* > 0$  on  $Y$  axis ( $\frac{\partial \varphi}{\partial X} = 0$ ), we get,

$$\frac{\varphi_{+1,0} - \varphi_{-1,0}}{2a_{t^*}h} = 0 \quad (4.44)$$

From equation (4.44), the unknown  $\varphi_{-1,j}$  on the fictitious boundary represented as dotted line in figure 4.2 is eliminated. Similarly, for any  $i$  when  $j = 0$ ,  $\varphi_{i,-1}$  is eliminated from the boundary condition at  $t^* > 0$ ,  $\frac{\partial \varphi}{\partial Y} = 0$  on  $X$ -axis.

Second, for grid points represented by small circles in figure 4.2, the step lengths are unequal and the situation around such a grid point is magnified in figure 4.3. The equation (4.43) is replaced by<sup>112</sup>,

$$\begin{aligned} \frac{2h^{-2}}{\left(\frac{a_{t^*}}{b_{t^*}}\right)^2} \left[ \frac{1}{(\lambda_i+1)} \varphi_{i-1,j} - \frac{1}{\lambda_i} \varphi_{i,j} + \frac{1}{\lambda_i(\lambda_i+1)} \varphi_{i+1,j} \right] + \\ 2k^{-2} \left[ \frac{1}{\lambda_j+1} \varphi_{i,j-1} - \frac{1}{\lambda_j} \varphi_{i,j} + \frac{1}{\lambda_j(\lambda_j+1)} \varphi_{i,j+1} \right] = 0 \end{aligned} \quad (4.45)$$



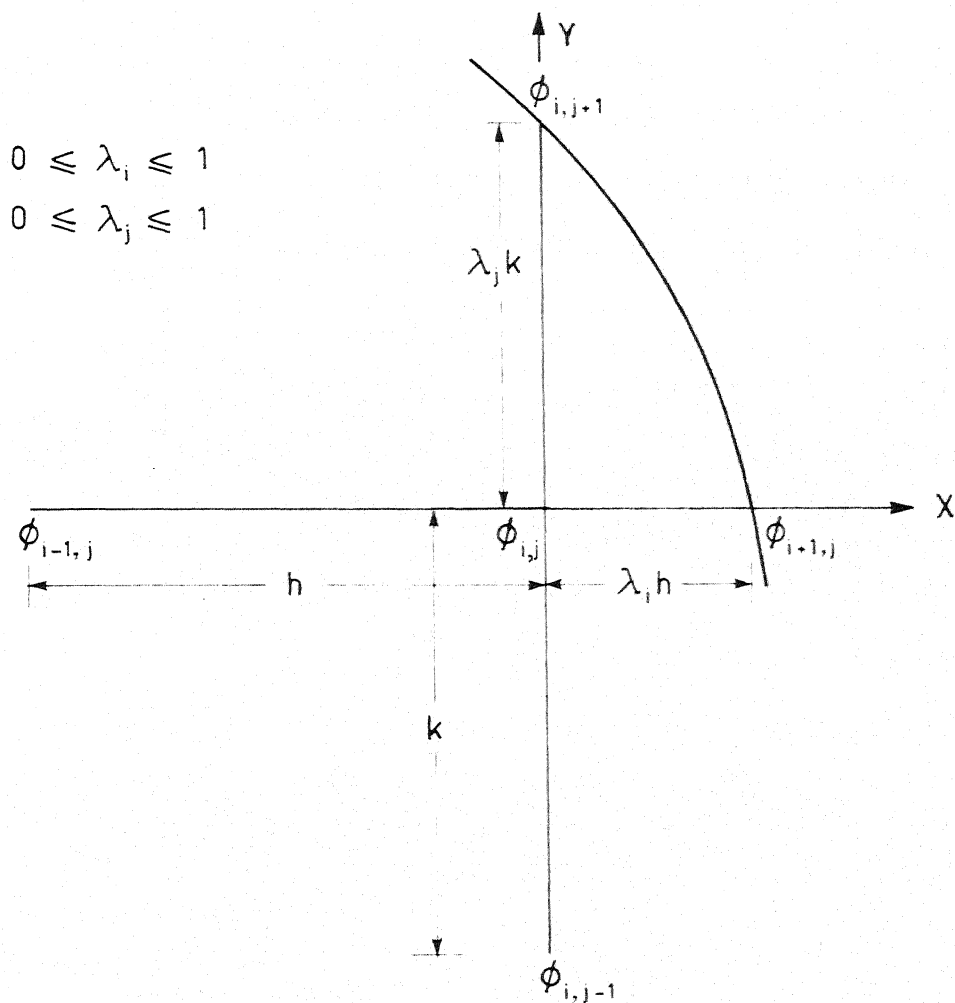


Fig. 4.3 Magnified view of the surroundings of a grid point near the boundary for solution of fluid flow equations.

It is to be noted that for  $\lambda_i = \lambda_j = 1$  equations (4.45) and (4.43) become identical. Using equations (4.43) and (4.45) for all  $i, j$ 's we get a set of algebraic equations which can be put in a matrix form. By using matrix iteration [Gauss iteration]<sup>99</sup> the  $\phi$  values at time  $(t^*+p)$  are evaluated, since the boundary values evaluated in step 2 are valid for time  $t^*+p$ .

[In the present problem the matrix iteration scheme converges. This can be shown as follows. The absolute value of a diagonal element in any row of the matrix as stated earlier is given by,

$$|\text{Diagonal element}| = \frac{2h^{-2}}{\left(\frac{a_{t^*}}{b_{t^*}}\right)^2} \left(\frac{1}{\lambda_i}\right) + 2k^{-2} \left(\frac{1}{\lambda_j}\right) \quad (4.46)$$

The absolute sum of off-diagonal elements

$$\begin{aligned} &= \frac{2h^{-2}}{\left(\frac{a_{t^*}}{b_{t^*}}\right)^2} \left[ \frac{1}{\lambda_i + 1} + \left\{ \frac{1}{\lambda_i(\lambda_i + 1)} \right\}^I \right] + \\ &\quad 2k^{-2} \left[ \frac{1}{\lambda_j + 1} + \left\{ \frac{1}{\lambda_j(\lambda_j + 1)} \right\}^{II} \right] \\ &= \frac{2h^{-2}}{\left(\frac{a_{t^*}}{b_{t^*}}\right)^2} \left(\frac{1}{\lambda_i}\right) + 2k^{-2} \left(\frac{1}{\lambda_j}\right) \quad (4.47) \end{aligned}$$

Near the boundary points either I or II or both terms will be transferred to the known vector side. Therefore, from equations (4.46) and (4.47) we get for the matrix,

Absolute value of diagonal element

$$\geq \text{Absolute sum of off-diagonal elements} \quad (4.48)$$

This (4.48) satisfies the condition for convergence of matrix iteration (Gauss-iteration)<sup>99</sup>].

Step 4 : Velocity components at time  $t^*+p$  are computed from  $\varphi_{i,j}$ 's as evaluated in Step 3 at time  $t^*+p$ . At the interior points  $u_{i,j}$  and  $v_{i,j}$  are computed by the following finite difference formula,

$$u_{i,j} = (2h a_{t*})^{-1} [\varphi_{i+1,j} - \varphi_{i-1,j}] \quad (4.49)$$

$$v_{i,j} = (2k b_{t*})^{-1} [\varphi_{i,j+1} - \varphi_{i,j-1}] \quad (4.50)$$

At the interior points as represented by small open circles in figure 4.2, due to unequal step lengths, the equations (4.49) and (4.50) are replaced by<sup>112</sup> (see figure 4.3),

$$u_{i,j} = (a_{t*}h)^{-1} \left[ -\frac{\lambda_i}{\lambda_i(\lambda_i+1)} \varphi_{i-1,j} - \frac{1-\lambda_i}{\lambda_i} \varphi_{i,j} + \frac{1}{\lambda_i(\lambda_i+1)} \varphi_{i+1,j} \right] \quad (4.51)$$

$$v_{i,j} = (b_{t^*k})^{-1} \left[ - \frac{\lambda_j}{\lambda_j(\lambda_j+1)} \varphi_{i,j-1} - \frac{1-\lambda_j}{\lambda_j} \varphi_{i,j} + \frac{1}{\lambda_j(\lambda_j+1)} \varphi_{i,j+1} \right] \quad (4.52)$$

At the boundary backward differences are employed to extrapolate the velocity components at points  $X_0, X_{0.1}, \dots, X_{0.9}$  and  $Y_0, Y_{0.1}, \dots, Y_{0.9}$  at time  $t^*+p$ , from  $\varphi_{i,j}$  values evaluated in previous steps (2 and 3).

Step 5 : Replacing time derivative of equation (4.41) by backward difference we get,

$$b_{t^*+p} = b_{t^*} + \tau_1^p v_{t^*+p} \Big|_{X=0} \quad (4.53)$$

where  $v_{t^*+p} \Big|_{X=0}$  is the velocity component evaluated at time  $t^*+p$  at the point  $X_0$  in Step 4. As the volume of the ellipsoid remains constant, using  $b_{t^*+p}$  as evaluated by equation (4.53), we get,

$$a_{t^*+p} = r^3 / b_{t^*+p}^2 \quad (4.54)$$

Since the potential drop between the two grains remains unchanged even after stretching, the field increases as a function of time. From figure 2.3 of Chapter 2 it can be shown that, at time  $t^*+p$ ,

$$E_{t^*+p} = E_0(s_0/s_{t^*+p}^*) \quad (4.55)$$

$$\text{where } s_{t^*+p} = s_0 - 2(a_{t^*+p} - r) \quad (4.56)$$

- Step 6 :  $t^* = t^* + p$  is set.
- Step 7 : Steps 2 to 6 are repeated, till  $t = 0.9$ .
- Step 8 : The difference between  $(s_0/2 - a_{t^*})$  is evaluated.
- Step 9 : Depending on whether difference is positive or negative, time  $t_1$  is increased or decreased.
- Step 10 :  $t_1$  in Step 1 is replaced by  $t_1$  in Step 9.
- Step 11 : Steps 1 to 10 are repeated. This process is continued until we get two values of  $t_1$  such that in one case the difference  $(s_0/2 - a_{t^*})$  is negative and in other case the difference is positive.
- Step 12 : Using the method of bisection  $t_1$  is evaluated and time  $t_1$  in Step 1 is replaced by this new value of  $t_1$ .
- Step 13 : Steps 1 to 8 and then Step 12 are repeated till the difference as evaluated in Step 8 is within  $\pm 0.1^{\circ}$  and the time which is evaluated in Step 12 is the required time.

The programme developed for the solution is given in Appendix 3. The programme is written in Fortran language with some features permitted in DEC System 1090 computer.

## 4.4 Experimental

### 4.4.1 Preparation of glass and blowing of thin film

A glass batch of composition  $80V_2O_5, 15P_2O_5, 5Bi_2O_3$  (mole %) has been melted. The melting is described in Section 3.3.1 of Chapter 3. The blowing of thin films used for pulse response measurement has been described in Section 3.3.2.1 of Chapter 3.

### 4.4.2 Pulse response measurement at room temperature

#### 4.4.2.1 Pulse circuit

Figure 4.4 shows block diagram of circuit configuration indicating the principle of pulse circuit operation. A standard pulse generator (Systronics Dual Channel, Model 1110-D) is used as a source of stimulus for providing a rectangular pulse of appropriate height and width to be impressed across the sample. However, the driving capacity in terms of power and current demanded by the sample of pulse generator is inadequate and therefore a buffer circuit combination consisting of Schmitt trigger interface and a solid state high speed (transistor) switch are interposed between the stimulus pulse generator and the sample. The regulated D.C. power supply (Aplab, Model 7152) is essential for providing the requisite supply voltages for proper biasing of Schmitt trigger and the power driver switch. In addition, it performs the essential function of determining the height or amplitude of final pulse that is applied across the sample. This is accomplished by varying the front panel DC

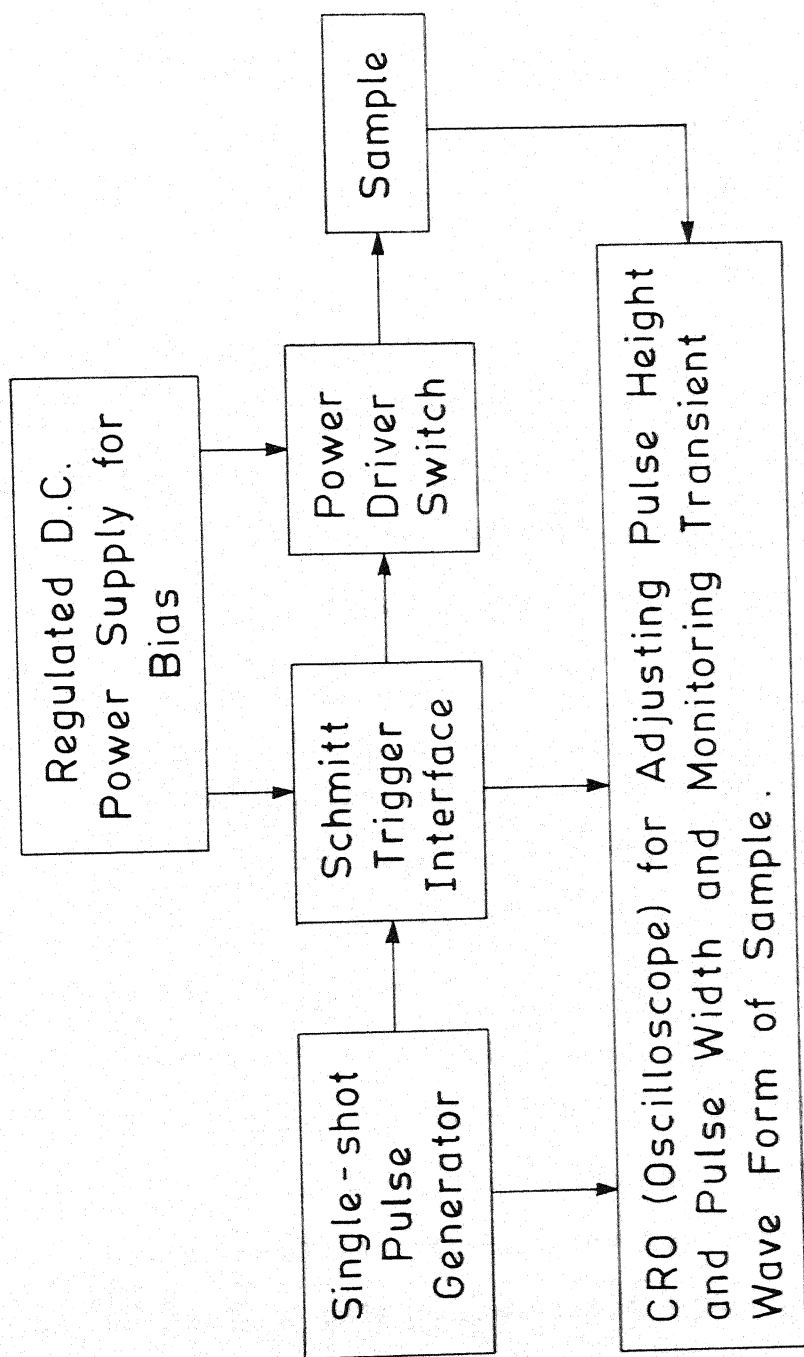
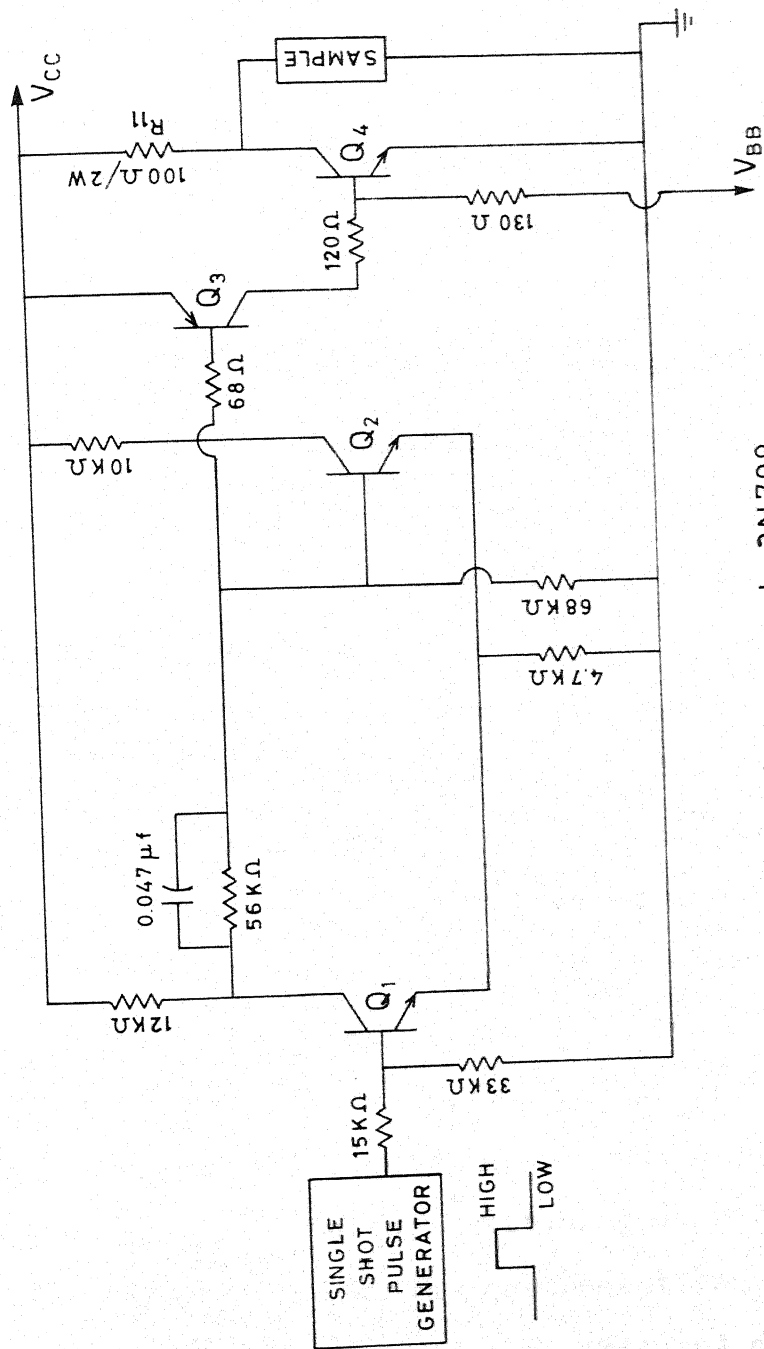


Fig. 4.4 Block diagram of circuit configuration showing principles of pulse circuit operation .

level control, provided on this equipment and monitoring it on the CRO which is also connected to the circuit at relevant mode for this purpose. The CRO made by Hewlett Packard (Model 1725A; 275 MHz) is a dual trace oscilloscope with delayed time base and digital volt/ohm meter.

Figure 4.5 shows the schematic representation of the circuit used for pulse response measurement. Transistor  $Q_4$  (ECN 055) is used as a shunt type of electronic switch and the current limiting resistor  $R_{11}$  is in series with the parallel combination of transistor  $Q_4$  and the sample. The positive DC supply voltage ( $V_{cc}$ ) is used for supply the pulsed current. When the input pulse to the base drive of  $Q_4$  turns it off from normally on-state, a pulse height of  $V_{cc}$  volts and duration of  $\tau$  seconds is impressed across the sample, consequently when the pulse height and width are correct the sample undergoes switching from the off to the on-state thereby conducting current of significant magnitude limited only by the series combination of resistor  $R_{11}$  and the sample in the on-state. Finally, on termination of pulse duration  $\tau$ , the presently off-transistor  $Q_4$  turns on again but this time shares the current in parallel with the low impedance of the switched sample. To apply a pulse which first turns off  $Q_4$  on its leading edge and then turns it back to the on-state  $\tau$  seconds later, the requisite base drive current is supplied by the pre-driver stage consisting of transistor  $Q_3$  (2N 2904) which in





- $Q_1, Q_2$  : Schmitt trigger transistors each 2N708  
 $Q_3, Q_4$  : Power driver switches ( $Q_3$ : 2N2904,  $Q_4$ : ECN055)  
 $V_{CC}$  : Positive DC regulated supply  
 $V_{BB}$  : Negative DC regulated supply

Fig. 4.5 Schematic representation of pulse circuit.

turn is driven by the composite combination of transistors  $Q_1$  (2N 708) and  $Q_2$  (2N 708) and associated components connected in Schmitt trigger configuration. The Schmitt trigger circuit ( $Q_1 + Q_2$ ) is a bistable regenerative switching circuit designed to buffer the pulse generator from the load of pre-driver and driver stages ( $Q_3 + Q_4$ ) and offers the additional important advantage of high speed switching action with improvement in the time of transitions on the leading and trailing edges.

#### 4.4.2.2 Measurement procedure

For measurement we have placed the thin film sample vacuum deposited with gold on two faces between two metallic electrodes housed in a measuring cell as described in Section 3.3.6.2 of Chapter 3. The rectangular pulse is provided by a standard dual pulse generator. The internal trigger is used to provide a direct output monitored on a high bandwidth delayed time base (275 MHz) dual trace CRO with sample disconnected from the circuit. This is necessary to obtain a recurrent pulse train on the CRO screen which is held stationary thereon enabling to adjust via pulse generator controls the width of the positive pulse position to the requisite magnitude prior to each switching operation. The precision and accuracy of pulse width measurement is enhanced by the availability of the feature of time interval mode capability built into the specific CRO. The height of pulse actually driving the sample is  $V_{cc}$ , being determined by the DC regulated supply

voltage. Next, mode of pulse generator is changed over to the manual trigger mode and the sample is connected to the circuit in shunt across the driver  $Q_4$ . Now using the push button microswitch of pulse generator a single shot pulse is injected into the circuit causing the driver to apply a single shot pulse drive across the sample so as to subject it to switching action. Finally the sample is disconnected from the circuit and its resistance is measured on a low voltage ohm meter (1V DC excitation) so as to determine whether the sample has switched from the off-state to the low resistance on-state (memory state). First we fix the pulse height at 5 volts and sequentially increase the pulse duration from 10 microseconds to a few hundred microseconds by suitable interval. Each time after passing a single pulse the sample is checked whether it has switched or not.

In the event of no switching taking place the pulse height is increased and the above sequence of experiments are repeated till the memory state is achieved.

#### 4.5 Results and Discussions

Figure 4.6 represents the stretching of semi-major axis of the ellipsoid in molten condition by the critical switching field as a function of time for bismuth metal of radius 150 Å and separation to diameter ratio 0.03. The time required to join up is  $9.5 \times 10^{-10}$  second. It is seen from the figure

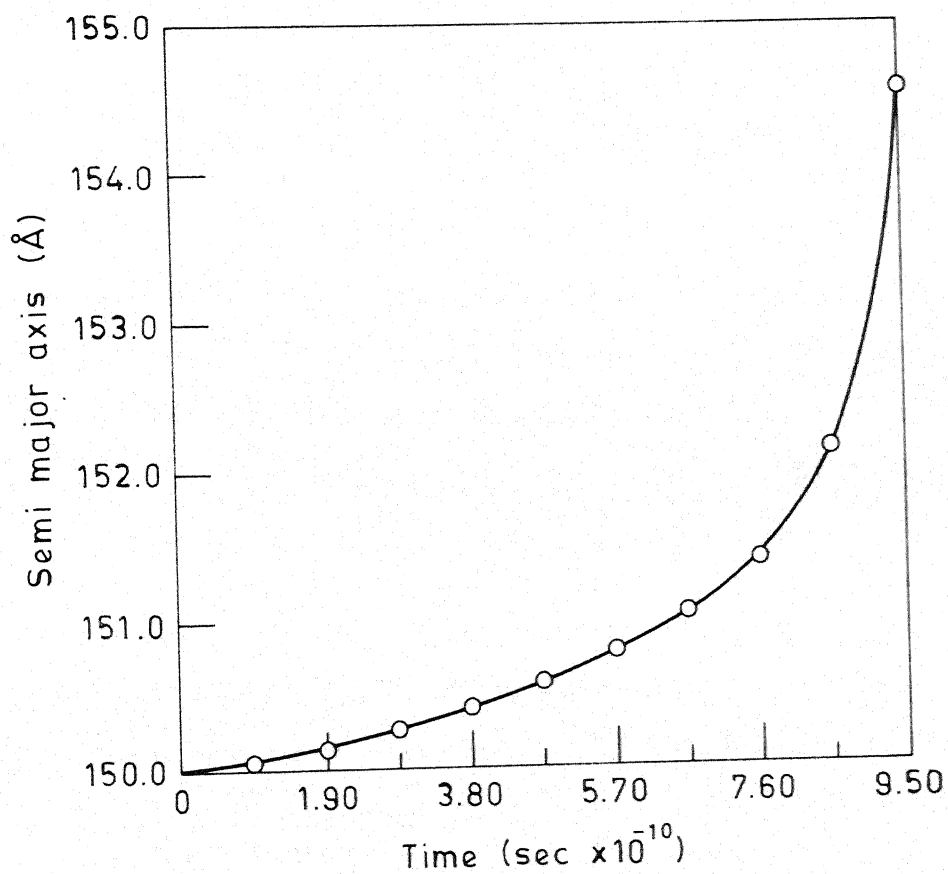


Fig. 4.6 Stretching of two neighbouring ellipsoids as a function of time under the influence of an electric field.

that initially the semi-major axis elongates slowly but later on at a rapid rate. This is because of the fact that as the distance between the two proximate grains decreases, the effective field increases (equation (4.55)) thereby causing a faster rate of deformation.

Table 4.1 gives the switching time ( $t_h$ ) as calculated from the solution of the time dependent heat equation in Chapter 3 and the time ( $t_s$ ) required for two proximate grains to coalesce as obtained from the solution of the fluid flow equations which has been described in this chapter for different diameters and separation to diameter ratios.

We observe that  $t_s$  remains almost constant for a particular diameter even if the  $s_0/d$  ratio increases. This arises due to the fact that a larger electric field is present in the latter case which lowered the time taken by the granules to stretch by the required amount. It is evident from the table 4.1 that  $t_s$  is less than  $t_h$  by approximately four orders of magnitude. Thus the stretching dynamics is much faster than the kinetics of the heating of the sample due to Joule losses. This, therefore, justifies the assumption made in Chapter 3 for the computation of I-V characteristics that once the required temperature profile is achieved within the sample, coalescence of proximate metallic granules takes place.

Table 4.2 gives a few typical values of switching time obtained by pulse experiments. These are found to have values

Table 4.1 Calculated switching time for a glass of composition  $80V_2O_5, 15P_2O_5, 5Bi_2O_3$  (mole%) for different d and  $(s_o/d)$  ratios

Particle diameter $\phi$ A	Separation to diameter ratio $(s_o/d)$	Switching time for sample of thickness 10 $\mu m$ $t_h \times 10^5$ sec.	Switching time as calculated from stretching of grains $t_s \times 10^9$ sec.
300	0.02	1.32	0.95
	0.03	0.72	0.95
	0.04	0.50	0.94
	0.05	0.36	0.94
	0.06	0.28	0.93
	0.07	0.23	0.93
400	0.02	7.39	1.46
	0.03	3.88	1.45
	0.04	1.82	1.45
	0.05	1.36	1.44
	0.06	1.07	1.43
	0.07	0.89	1.43
500	0.02	-	2.03
	0.03	5.01	2.03
	0.04	2.88	2.02
	0.05	2.05	2.01
	0.06	1.59	2.01
	0.07	1.29	2.00
600	0.02	-	2.69
	0.03	8.49	2.68
	0.04	4.15	2.67
	0.05	3.41	2.66
	0.06	2.12	2.65
	0.07	1.72	2.64

---

700	0.02	-	3.38
	0.03	18.46	3.36
	0.04	5.86	3.35
	0.05	3.69	3.33
	0.06	2.72	3.32
	0.07	2.16	3.31
800	0.02	-	4.13
	0.03	-	4.10
	0.04	8.60	4.10
	0.05	4.82	4.08
	0.06	3.42	4.06
	0.07	2.65	4.04
900	0.02	-	4.92
	0.03	-	4.90
	0.04	-	4.88
	0.05	6.36	4.86
	0.06	4.27	4.85
	0.07	3.23	4.83
1000	0.02	-	5.76
	0.03	-	5.74
	0.04	-	5.72
	0.05	8.63	5.69
	0.06	5.31	5.68
	0.07	3.90	5.65

---

Table 4.2 Comparison of experimentally determined switching time and switching field under pulse measurement with those theoretically calculated for a glass composition  $80V_2O_5, 15VP_2O_5, 5Bi_2O_3$  (mole %)

Experimental switching field $V/cm \times 10^{-4}$	Pulse	$E_m^b$ /calc. $V/cm \times 10^{-4}$	Experimental switching time $\times 10^5$ sec.	Switching time	
				$t_h \times 10^5$ sec. (calc.)	$t_s \times 10^9$ sec. (calc.)
0.63	3.8	0.46 ( $d=300\text{\AA}, s_0/d=0.02$ )	6.0	1.32 ( $d=300\text{\AA}, s_0/d=0.02$ )	0.95 ( $d=300\text{\AA}$ )
		0.87 ( $d=300\text{\AA}, s_0/d=0.03$ )		0.72 ( $d=300\text{\AA}, s_0/d=0.03$ )	
		1.30 ( $d=300\text{\AA}, s_0/d=0.04$ )		7.39 ( $d=400\text{\AA}, s_0/d=0.02$ )	1.46 ( $d=400\text{\AA}$ )
2.5	5.0	0.72 ( $d=400\text{\AA}, s_0/d=0.03$ )	5.0		



around 50-60 microseconds. The last two columns include the switching times  $t_h$  and  $t_s$  respectively taken from columns 3 and 4 of table 4.1. Columns 1 and 2 of table 4.2 give the switching fields as obtained by DC (from figure 3.6 of Chapter 3) and pulse measurements respectively. In column 3 of table 4.2, the theoretically calculated switching fields (taken from column 6 of table 2.1 of Chapter 2) are given.

Comparing columns 4 and 5 of table 4.2 we see that the calculated  $t_h$  is in agreement within order of magnitude of the experimental switching time for particles of diameters 300 Å and 400 Å with separation to diameter ratios of 0.02 and 0.03.

However,  $t_s$  is much smaller as compared to the experimental value. Hence, switching at room temperature is controlled by the Joule heating step as we have mentioned earlier. However, it is possible in principle to get a switching speed of the order of nano-seconds provided the metallic particles are in the molten state.

Comparing columns 1,2 and 3 of table 4.2 we see that experimental switching fields (DC and pulse) are within order of magnitude of the predicted fields for particles of diameters 300 Å and 400 Å with separation to diameter ratios of 0.02, 0.03 and 0.04. The differences in the switching fields as measured under DC and pulse conditions are attributed to the variation in microstructure depending on the melting and the blowing conditions of glasses. This agreement is reasonable

in view of the fact that a number of simplifying assumptions have been made in developing the model in Chapter 2.

It is necessary to raise the temperature to the melting point of bismuth so that the molten metallic bismuth granules can be stretched under the action of an electric field. It has been shown in Chapter 2 that the critical electric field for heating is less than the critical field for memory switching. Thus the electric field applied will raise the temperature level within the material to a value much higher than what is required for melting of bismuth granules. As the temperature increases the glass structure becomes more open and also due to the fact that  $V_2O_5$ - $P_2O_5$ - $Bi_2O_3$  glasses are fairly low melting it is believed that the resistance offered by the matrix to the stretching of molten bismuth particles will be small as compared to the surface tension forces. We have, therefore, neglected any such opposing force by the glass matrix to the granule deformation in our analysis.

## CHAPTER 5

### OPTICAL PROPERTIES OF VANADIUM PHOSPHATE AND SILICATE GLASSES CONTAINING BISMUTH GRANULES

#### 5.1 Introduction

Colloidal suspensions in glasses scatter light. Colloids of large particle size and sufficient concentration can generate turbidity in the glass which is undesirable. Therefore, to induce interesting optical properties highly absorbing materials are needed to predominate over the scattering. Metals being highly absorbing meet this condition provided the particle sizes are kept below 50 nm. Therefore, a proper choice of glass compositions and control of melting conditions can lead to the formation of ultrafine metal particles in a glassy matrix.

Doremus<sup>113,114</sup> has studied the optical absorption of photosensitive alkali aluminoborosilicate glasses containing gold and silver. The latter are precipitated in the colloidal form by UV radiation followed by a suitable heat treatment. The spectral dependence of optical absorption has been analysed by Mie theory. In the case of glass containing gold the correspondence between theory and experiment is good while in the other case the measured absorption compares reasonably well with that predicted by Mie theory with regard to the shape and position of the absorption peak.

Yellow, amber and red colours can be induced in the glasses by the process of staining. In this process compounds of silver or copper or a mixture of these are applied on the surface of the glass. Then the coated glass is baked to a temperature in the range of annealing so that silver and copper undergo ion-exchange with the alkali metal-ions. The subsequent reduction treatment induces metallic colloids within the surface of the glass by nucleation and growth. The optical absorption of the borosilicate glass (composition similar to 'Pyrex') stained with copper and a mixture of copper and silver has been studied by Rawson<sup>115</sup>. Mie theory has been used to quantitatively account for the spectral transmission curve in the range of 0.4 to 0.8  $\mu\text{m}$ . The quantitative agreement between the calculated and the experimental transmission is good for glasses stained with copper alone, but the agreement is less satisfactory when a mixture of copper and silver is present. This deviation is attributed to the formation of copper-silver alloy particles.

Chakravorty et al.<sup>116</sup> have studied the optical absorption of the float glass which has been subjected to ion-exchange with copper salt followed by reduction. The ion-exchange and reduction produce metallic copper within the surface of the glass. The characteristic absorption bands have been explained by Maxwell-Garnett theory. Recently, optical studies in the visible range have been carried out on alkali containing

C-glasses and borosilicate glasses which have been subjected to ion-exchange in molten  $\text{AgNO}_3$  followed by a reduction treatment in hydrogen gas at different temperatures and for various time periods<sup>117</sup>. The absorption peak position has been explained on the basis of Maxwell-Garnett effective medium theory.

The optical properties of cermet films produced by co-sputtering or evaporation (see Section 1.6 of Chapter 1) have also been studied extensively. The early measurement of optical properties of evaporated  $\text{Au/SiO}_2$  cermet films in the range  $0.4 < \lambda < 0.7$  has been reported by Hampe<sup>118</sup>. Cohen et al<sup>119</sup> have investigated in details the optical properties of co-sputtered  $\text{Ag/SiO}_2$  and  $\text{Au/SiO}_2$  cermet films in the entire range of  $0.2 \mu\text{m}$  to  $1.7 \mu\text{m}$ . Lissberger et al,<sup>120,121</sup> have studied the optical properties of  $\text{MgF}_2/\text{Au}$  and  $\text{Co/MgF}_2$  in the range of  $0.4 < \lambda < 0.6 \mu\text{m}$ .

Granqvist et al.<sup>122</sup> have studied the optical properties of ultrafine gold particles produced by evaporation of pure gold in presence of air at a few torr. The percent transmission shows a characteristics transmittance dip at around  $0.6 \mu\text{m}$ . Extensive computer calculations have been carried out based on the effective medium theories of Maxwell-Garnett as extended by Polder and van Santen (MG-PvS), of Hunderi (HU) and of Bruggeman (BR) to explain the spectral dependence of optical absorption. It has been shown that in the limit of low

concentration of metal all the above effective medium theories predict the same result. By invoking the dipole-dipole interaction between the metallic particles a better quantitative agreement has been achieved. The dipole-dipole interaction has been accounted for approximately by a set of effective depolarisation factors. Further assuming that the microstructure consists of certain fractions of spheres, f.c.c. clusters and single strand chains quantitative agreement within a few percent has been obtained. In the case of ultrafine aluminium produced by evaporation in a gas mixture of helium and oxygen, the optical transmission characteristics have been explained within the MG formalism by suitably incorporating the dipole-dipole interaction and size dependent dielectric permittivity of metal particles coated with oxide.<sup>123</sup> However the transmission dip occurring at  $0.85 \mu$  is much less compared to the theoretically predicted one. This has tentatively been ascribed to defect scattering within the metal particles. Similarly, the optical properties of metal-dielectric<sup>35, 124-126</sup> composites formed by evaporation of metals - nickel, chromium, silver and gold have been interpreted by using effective medium theories.

Abeles and Gittleman<sup>127</sup> have studied the insulator rich Ag/SiO<sub>2</sub> cermet films and by applying MG theory they conclude that the latter is superior to BR theory to explain the data. However, Granqvist et al.<sup>128</sup> have studied the applicability of MG-PvS, HU and BR theories on the experimental data of

Cohen et al.<sup>119</sup>. It has been found that no single effective medium theory can explain the experimental transmittance dip. However, this feature can at least be explained qualitatively by incorporating the distribution of depolarisation factors in the MG type of effective medium theory. Optical properties of co-sputtered  $\text{Cr}_2\text{O}_3/\text{Cr}$ <sup>33</sup>,  $\text{MgO}/\text{Au}$ <sup>32</sup> and co-evaporated  $\text{Ni}/\text{Al}_2\text{O}_3$ <sup>34</sup> have been investigated with a view to study the suitability of their application to photothermal conversion. Craighead et al.<sup>34</sup> have found a good correspondence between the prediction of MG theory and the optical absorption data of  $\text{Ni}/\text{Al}_2\text{O}_3$  cermet films. Granqvist<sup>129</sup> has carried out theoretical analysis based on MG and BR effective medium theories on the experimental optical data of  $\text{MgO}/\text{Au}$ <sup>32,130</sup>,  $\text{Al}_2\text{O}_3/\text{Au}$ <sup>131</sup> and  $\text{MgF}_2/\text{Au}$ <sup>120</sup>. The analysis shows that BR theory is superior to MG formalism in  $\text{Au}/\text{MgO}$  and  $\text{Au}/\text{Al}_2\text{O}_3$  cermet films but no such definite conclusion can be drawn in the case of  $\text{MgF}_2/\text{Au}$  cermet systems. Granqvist et al.<sup>132,133</sup> have carried out extensive computer calculations based on effective medium theories and applied to the case of silver in glassy matrix<sup>134,135</sup> and to the  $\text{Cr}/\text{Cr}_2\text{O}_3$ <sup>33</sup> cermet system.

Compared to an extensive investigation on the optical properties of metal-dielectric composite systems produced by sputtering or evaporation, such studies on glasses containing metallic granules are few. In this chapter we report on the characterisation of optical properties of oxide glasses

containing bismuth granules of dimensions of the order of a few hundred angstroms. Analyses of the type used in the case of cermet films have been applied extensively in the present investigation.

## 5.2 Experimental Procedure

### 5.2.1 Glass preparation and making of films

The glass compositions which have been investigated for optical studies are given in table 5.1.

The melting and preparations of thin films for first three glasses are similar to those discussed in Section 3.3.1 and 3.3.2.1 of chapter 3. Glasses 4,5 and 6 have been prepared from reagent grade chemicals.  $B_2O_3$  has been added as  $H_3BO_3$ ,  $Na_2O$  as  $Na_2CO_3$ , and  $SiO_2$  and  $Bi_2O_3$  have been introduced as their oxides. The glass batch is accurately weighed, thoroughly mixed in acetone and melted in a hard fired alumina crucible in an electrically heated furnace in the temperature range of  $1300^{\circ}C$  to  $1400^{\circ}C$ . After homogenisation, the films of glasses are prepared by blowing as discussed in Section 3.3.2.1 of Chapter 3.

### 5.2.2 Reduction of thin films

Figure 5.1 shows the reduction furnace schematically. A pyrex tube closed at both ends is inserted through the mullite muffle of an electrically heated furnace. R represents



Table 5.1 Compositions of glasses

Glass No.	Composition in mole percent					
	$V_2O_5$	$P_2O_5$	$SiO_2$	$B_2O_3$	$Na_2O$	$Bi_2O_3$
1	80	20	-	-	-	-
2	80	15	-	-	-	5
3	70	20	-	-	-	10
4	-	-	64	26	10	-
5	-	-	64	18	10	8
6	-	-	64	14	10	12

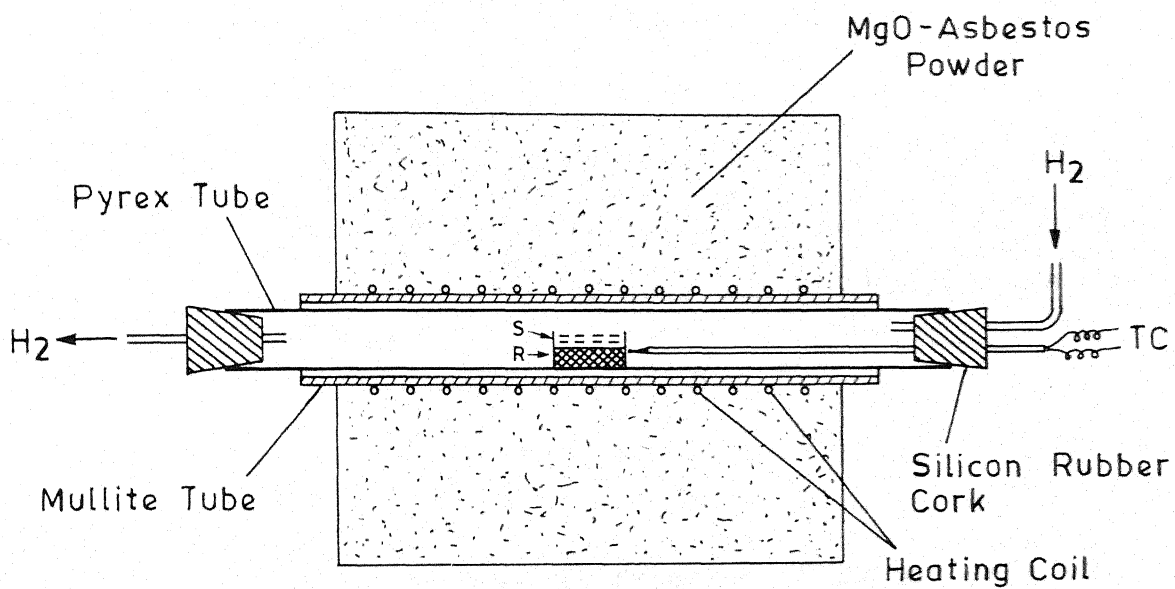


Fig. 5.1 Reduction furnace .

a refractory block on which the thin glass films S sandwiched between perforated metallic sheets are placed. A thermocouple TC is placed near the sample and is connected to an Aplan temperature controller. The reduction treatment has been carried out by passing hydrogen at a rate of 100 c.c./minute. Glasses no. 2 and 3 of the  $V_2O_5$ - $P_2O_5$ - $Bi_2O_3$  system have been reduced at  $200^\circ C$  for 1.0 hour and 2.0 hours respectively whereas the glass no. 5 and 6 of the  $Na_2O$ - $B_2O_3$ - $SiO_2$ - $Bi_2O_3$  system have been reduced at  $300^\circ C$  for the duration of 1.0 hour and 1.5 hours respectively.

### 5.2.3 Transmission electron microscopic studies

The technique for electron microscopic sample preparation has been described in Section 3.3.5 of Chapter 3. The microstructure and selected area diffraction (SAD) patterns of all virgin and reduced glasses containing bismuth have been taken by using Phillips EM 301 Electron Microscope. The SAD patterns have been analysed in a manner similar to that discussed in Section 3.3.5.

#### 5.2.3.1 Average particle size determination

For each sample a number of electron micrographs have been taken. A few hundred particles are measured. Then using the following formulae the average particle size and standard deviation have been calculated.

$$\bar{x} = \frac{\sum_{j=1}^n x_j n_j}{N} \quad (5.1)$$

$$s = \left[ \sum_{j=1}^N (x_j - \bar{x})^2 / (N-1) \right]^{1/2} \quad (5.2)$$

where  $x_j$  and  $n_j$  are respectively the mean particle size and frequency of the  $i$ th interval,  $n$  and  $N$  are the number of intervals and the total number of particles respectively.  $s$  is the standard deviation.

#### 5.2.3.2 Calculation of volume fraction

Assuming the precipitation of particles to be homogeneous throughout the glass matrix, we have used the point counting method to estimate the volume fraction ( $f_c$ ) by the following expression<sup>136</sup>,

$$f_c = \frac{n'}{N'} \quad (5.3)$$

where  $n'$  and  $N'$  are respectively the number of cross points coinciding with the particles and the total number of points present in the selected area of the transparent graph paper. However, the volume fraction calculated by this method is greater than the actual one because of the superimposition of all the particles across the thickness on the two dimensional electron microphotograph. Assuming the particles to be spherical the actual volume fraction  $f$  of the particles can be related to  $f_c$  by the following expression ,

$$f = \frac{2}{3} f_c \left( \frac{\bar{x}}{t_{em}} \right) \quad (5.4)$$

where  $t_{em}$  is the thickness of electron microscopic sample.

#### 5.2.4 Optical absorption studies

For studying the optical absorption the thin glass films have been sandwiched between two hard papers each having a square hole of about 5 mm x 5 mm punched in it. The optical spectra of virgin as well as reduced  $V_2O_5$ - $P_2O_5$ - $Bi_2O_3$  glasses (glass no. 2 and 3) have been taken in the visible range using base glass no.1 as the reference, while for  $Na_2O$ - $B_2O_3$ - $SiO_2$ - $Bi_2O_3$  glasses (glass no. 5 and 6), base glass no.4 has been used as reference. The spectra for the base glasses (glass no. 1 and 4) have been taken using air as the reference. All the spectra have been measured using Carry 17D Spectrophotometer.

##### 5.2.4.1 Calculation of optical absorption coefficient, $\alpha$

Carry 17D plots the optical density (O.D.) as a function of wavelength  $\lambda$ . From this curve at any wavelength we get,

$$(O.D.)_{\text{sample}} = (O.D.)_{\text{observed}} + (O.D.)_{\text{reference}} \quad (5.5)$$

From Beer-Lambert's law which relates optical density to absorption coefficient  $\alpha$ , we get,

$$\alpha = \frac{2.303[(O.D.)_{\text{observed}} + (O.D.)_{\text{reference}}]}{t_{\text{sample}}} \quad (5.6)$$

where  $t_{\text{sample}}$  represents the thickness of the sample.

#### 5.3 Results

Figures 5.2(a) and (b) show the plots of optical density as a function of wavelength in the visible range for vanadium

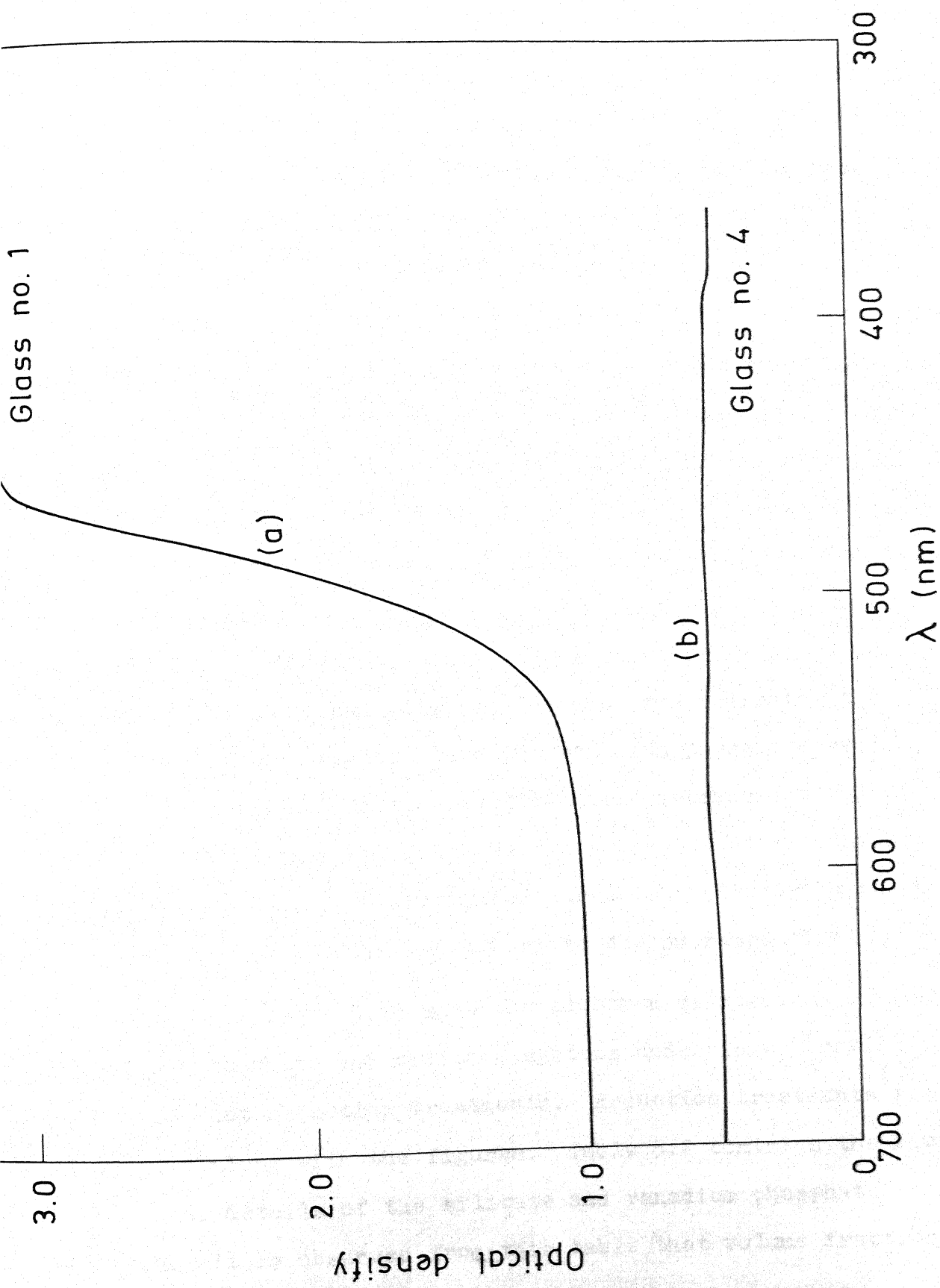


Fig. 5.2 Optical density as a function of wavelength for base glasses

phosphate base glass no.1 and silicate base glass no.4 respectively. While glass no.1 shows an absorption edge, the glass no.4 is featureless. Figure 5.3 represents the plots of optical absorption coefficients as a function of wavelength for glass no.2 and 3. Different reduction treatments applied to these glasses are indicated on the curves. It is observed that as the reduction time is increased for the same amount of bismuth in the glass compositions the absorption coefficients increase. The absorption peaks for glass no.3 subjected to different heat treatments occur at the same wavelength 440 nm, while for glass no.2 they occur in the range of 450-460 nm. Figure 5.4 represents the plots of  $\alpha$  values as a function of wavelength for glass no.5 and 6 for different reduction treatments. The arrow head attached to the curve indicates the scale of  $\alpha$  to the right. Like the vanadium phosphate system, it is observed that as the reduction time increases  $\alpha$  values for both glass no.6 and glass no.5 increase. Unlike vanadium phosphate system, each absorption curve shows two broad peaks in the range 500-530 nm and 420 nm to 430 nm respectively.

Figures 5.5 to 5.16 show the electron micrographs of the vanadium phosphate and silicate systems under investigation for different reduction treatments. Reduction treatments are indicated along with the figures. Table 5.2 contains the microstructural details of the silicate and vanadium phosphate glasses. It is observed from this table that volume fraction of

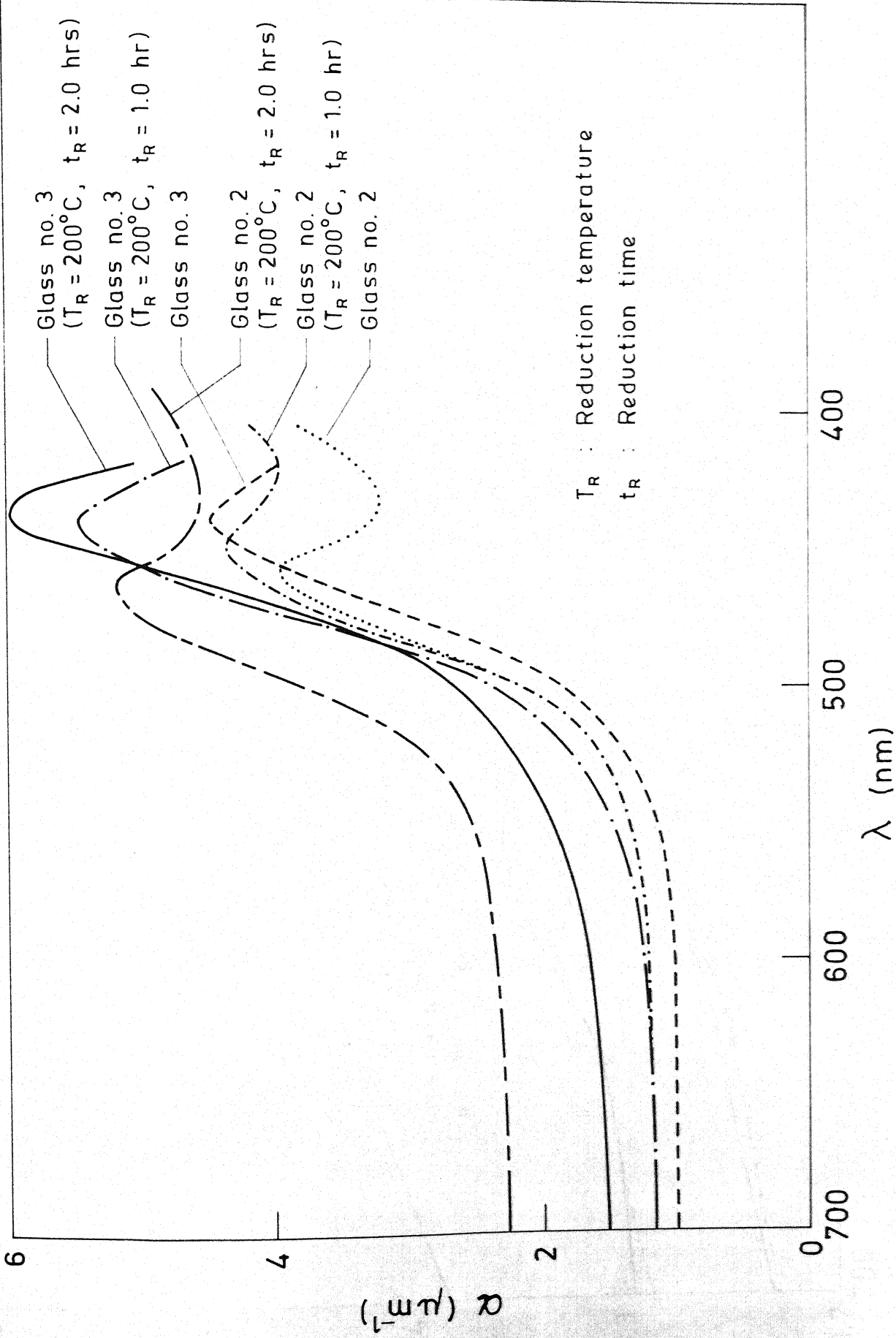


Fig. 5.3 Absorption coefficient  $\alpha$  as a function of wavelength  $\lambda$  for  $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$  glasses containing bismuth.



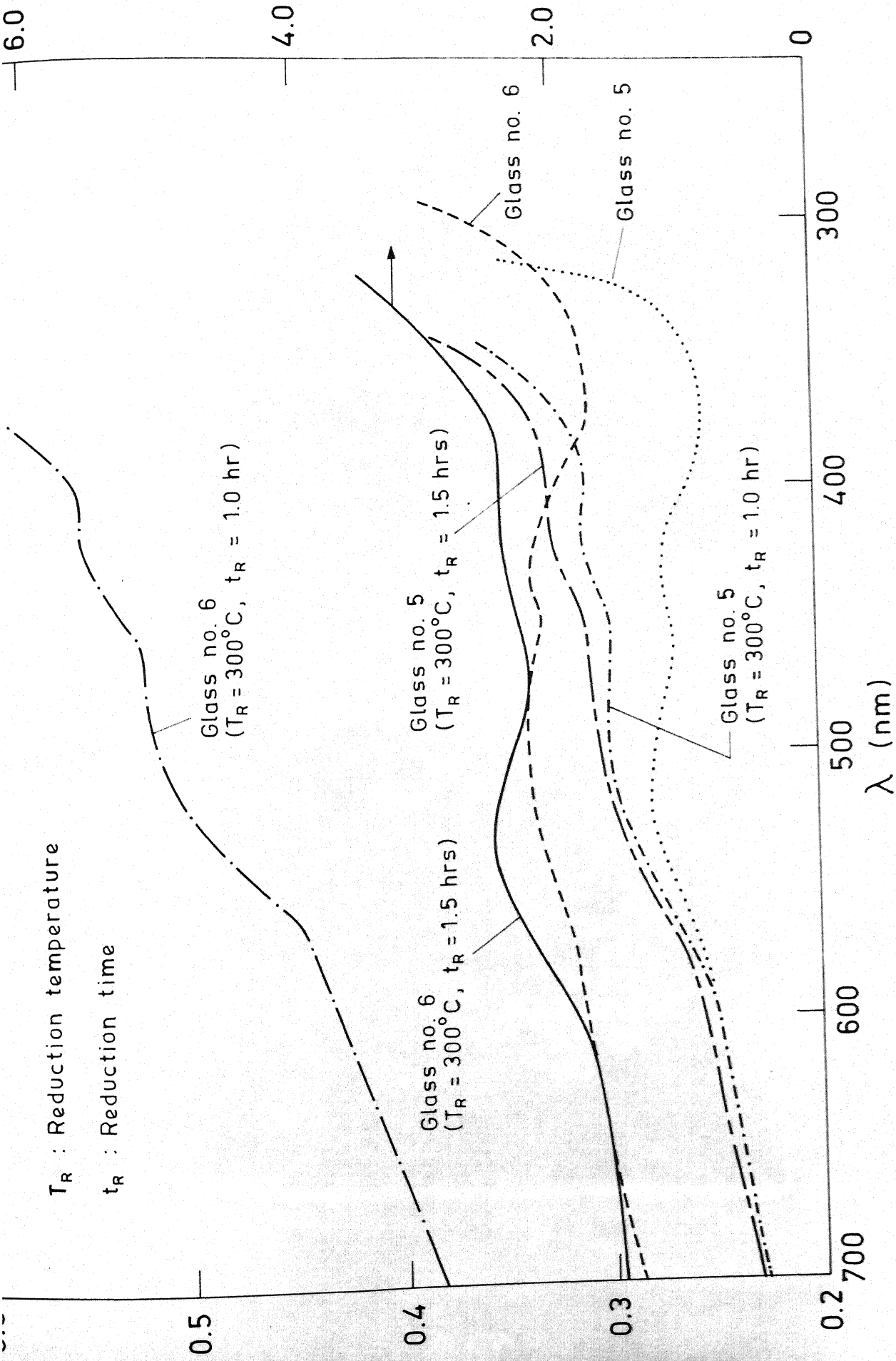


Fig. 5.4 Absorption coefficient  $\alpha$  as a function of wavelength  $\lambda$  for silicate

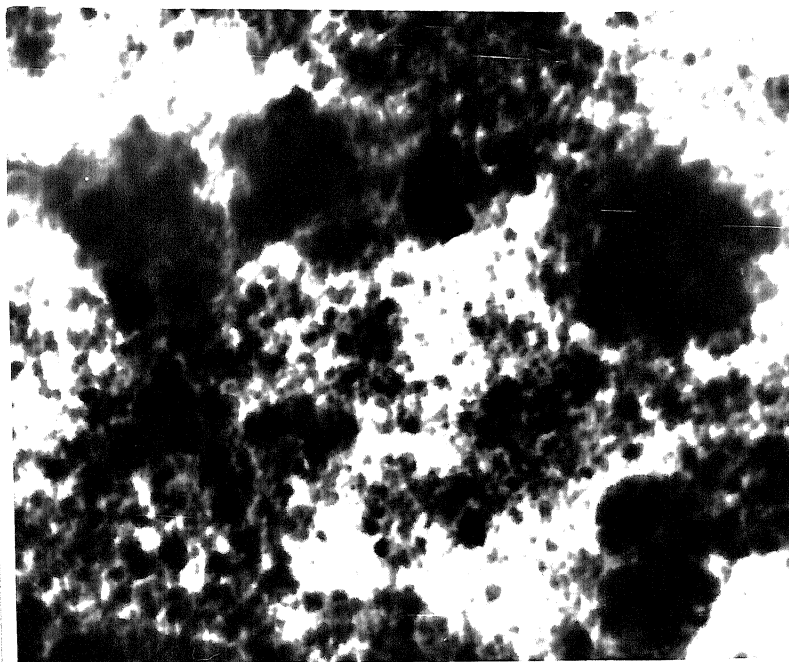


Fig.5.5 Electron micrograph of a sample of  
glass no.2  
X 117,000

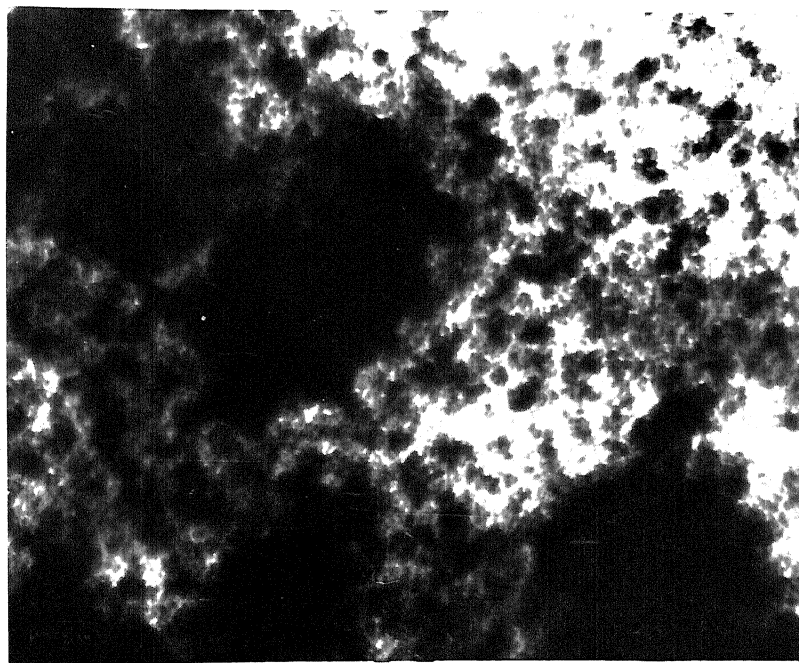


Fig.5.6 Electron micrograph of a sample of  
glass no.2 reduced at 200°C for  
1.0 hour  
X 84,000

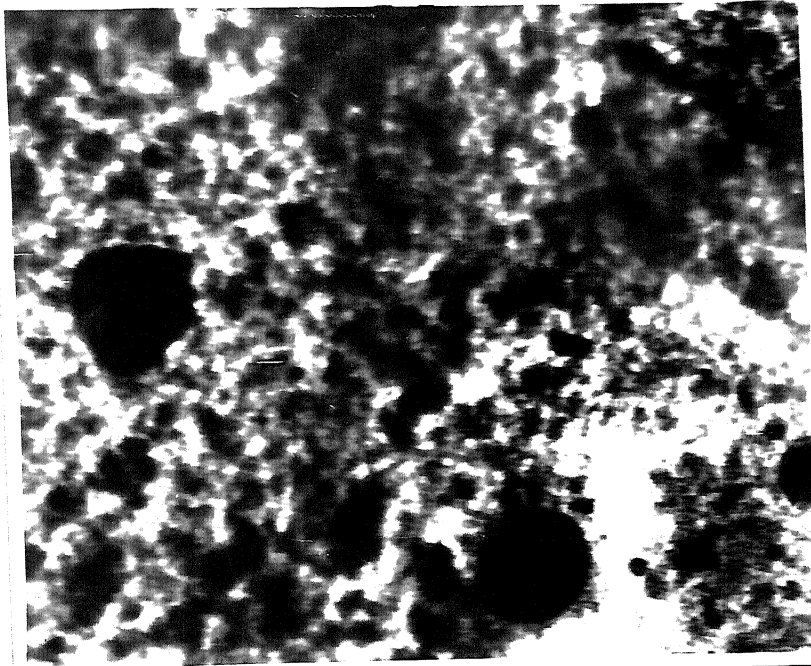


Fig.5.7 Electron micrograph of a sample of  
glass no.2 reduced at 200°C for  
2.0 hours  
X 84,000



Fig.5.8 Electron micrograph of a sample of  
glass no.3  
X 84,000

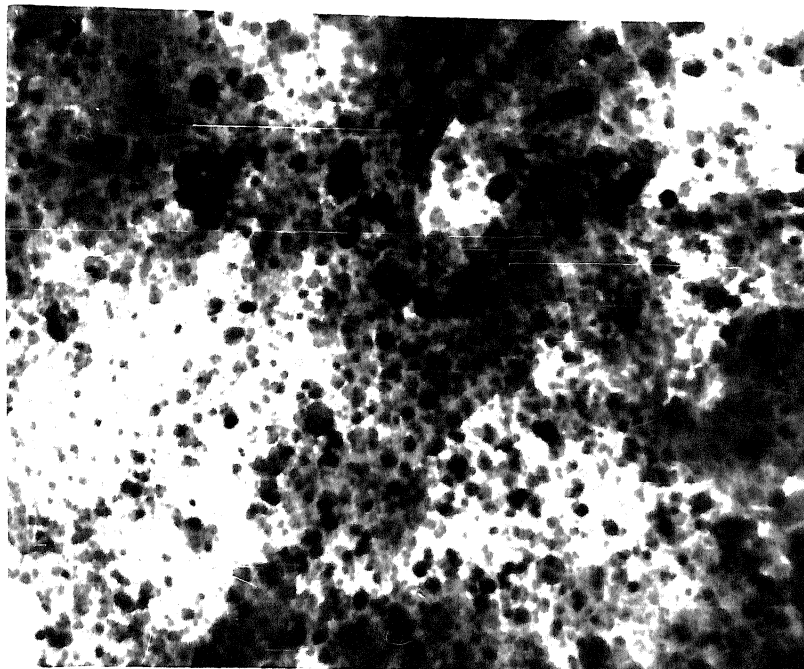


Fig.5.9 Electron micrograph of a sample of  
glass no.3 reduced at 200°C for  
1 hour  
X 84,000

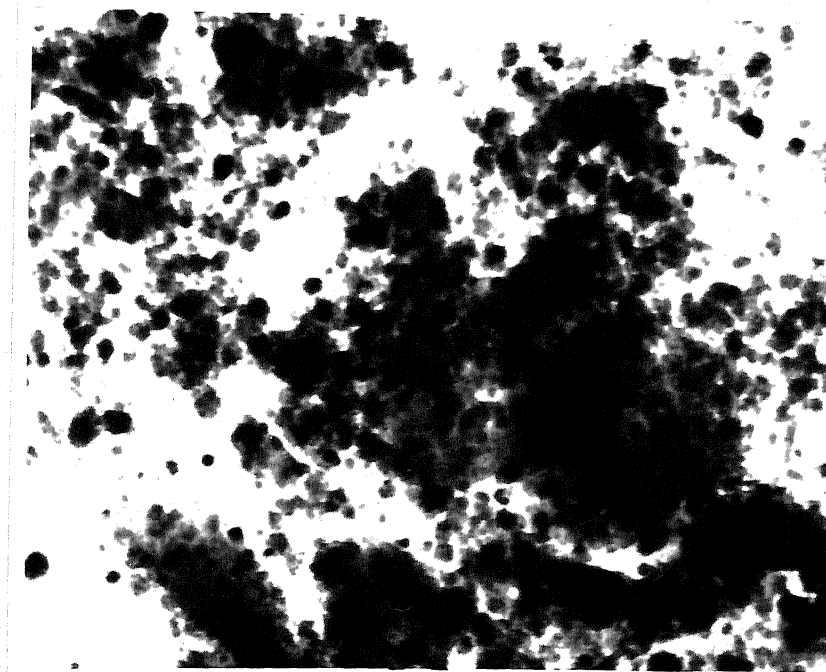


Fig.5.10 Electron micrograph of a sample of  
glass no.3 reduced at 200°C for  
2.0 hours  
X 84,000



Fig.5.11 Electron micrograph of a sample of  
glass no.5  
X 117,000

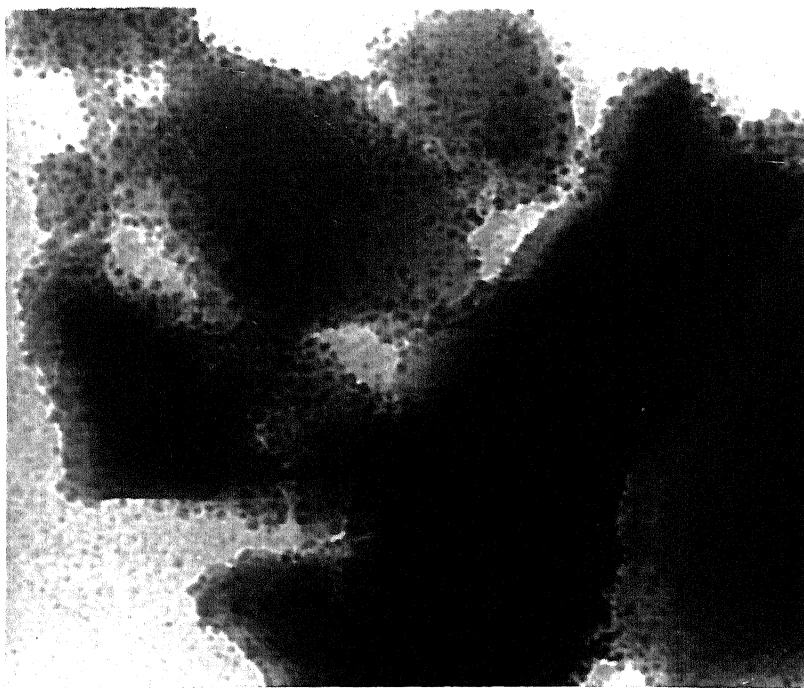


Fig.5.12 Electron micrograph of a sample of  
glass no.5 reduced at 300°C for 1 hour  
X 117,000



Fig.5.13 Electron micrograph of a sample of  
glass no.5 reduced at 300°C for  
1.5 hours  
X 117,000

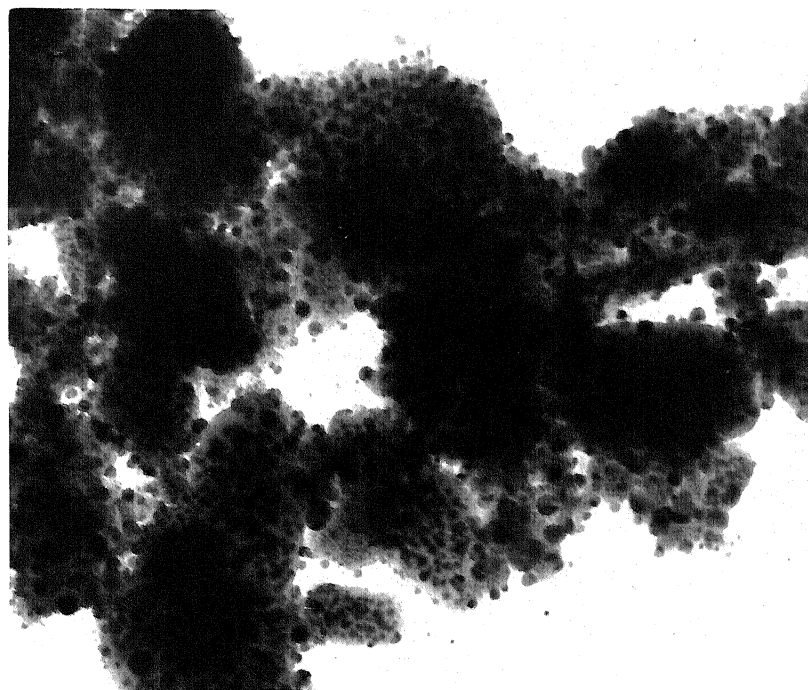


Fig.5.14 Electron micrograph of a sample of  
glass no.6  
X 66,000

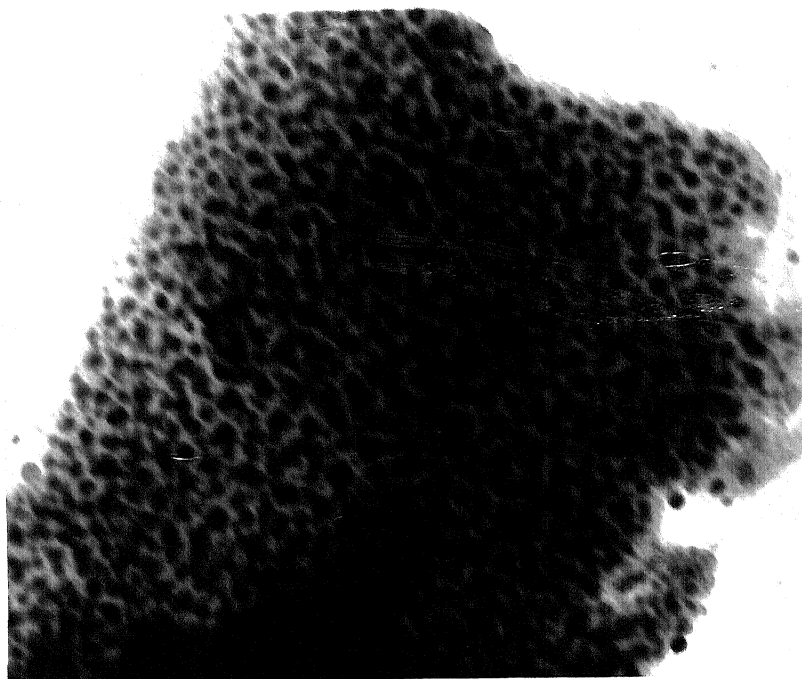


Fig.5.15 Electron micrograph of a sample of  
glass no.6 reduced at 300°C for  
1.0 hour  
X 117,000

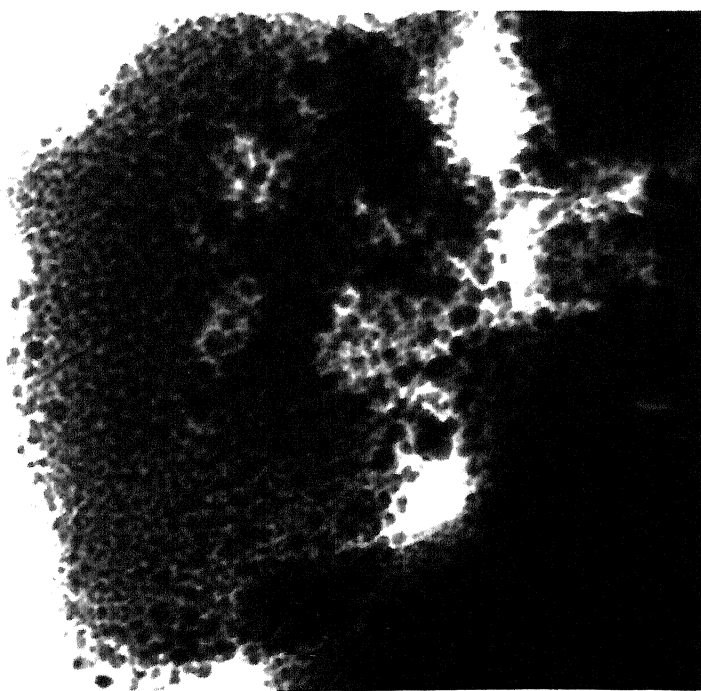


Fig.5.16 Electron micrograph of a sample of  
glass no.6 reduced at 300°C for  
1.5 hours  
X 117,000



Table 5.2 Microstructural parameters for different glasses under various reduction treatments

Glass System		$V_2O_5-P_2O_5-Bi_2O_3$			$SiO_2-B_2O_3-Na_2O-Bi_2O_3$								
Glass No.		2			3			5			6		
Reduction Treatment		200			200			200			300		
T		1			1			2			1		
t		2			2			1			1.5		
		200			200			300			300		
		200			200			300			300		
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		200			200			300			300		
		200			200			300			300		
		200											



for glass no.2 and 3 varies in the range 0.01 to 0.04 and the average diameter varies in the range 75 to 155 angstroms. For the silicate glasses  $f$  varies in the range 0.02 to 0.05 and the average particle size varies in the range of 80-160 angstroms.

Figures 5.17 and 5.18 show the SAD patterns of vanadium phosphate system for glass no.2 and glass no.3 reduced at  $200^{\circ}\text{C}$  for 2 hours respectively. Figures 5.19 and 5.20 show the SAD patterns for glass no.5 reduced at  $300^{\circ}\text{C}$  for 1.5 hours and glass no.6 respectively. Tables 5.3 to 5.6 give the calculated interplanar spacings ( $d_{hkl}$ ) from figures 5.17 to 5.20 respectively. Standard  $d_{hkl}$  values of metallic bismuth<sup>108</sup> have been included in each table for comparison. In  $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$  system (figures 5.5 - 5.10) globular structure is more prominent in figures 5.8 and 5.9, while in silicate system (figures 5.11 - 5.16) globular structure is more pronounced except in figures 5.15 and 5.16. However, in all figures certain fractions of interconnected chains are discernible.

#### 5.4 Discussions

Before discussing experimental results as given in the last section we briefly describe the salient features of the different theories available for explaining the optical behaviour of inhomogeneous materials.



Fig.5.17 Electron diffraction pattern of a sample of glass no.2

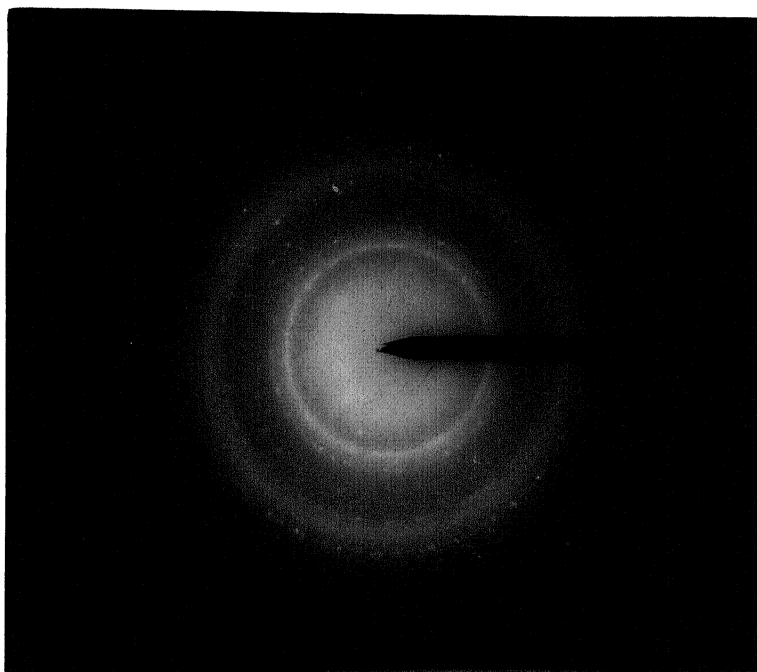


Fig.5.18 Electron diffraction pattern of a sample of glass no.3 reduced at 2000C for 2 hours

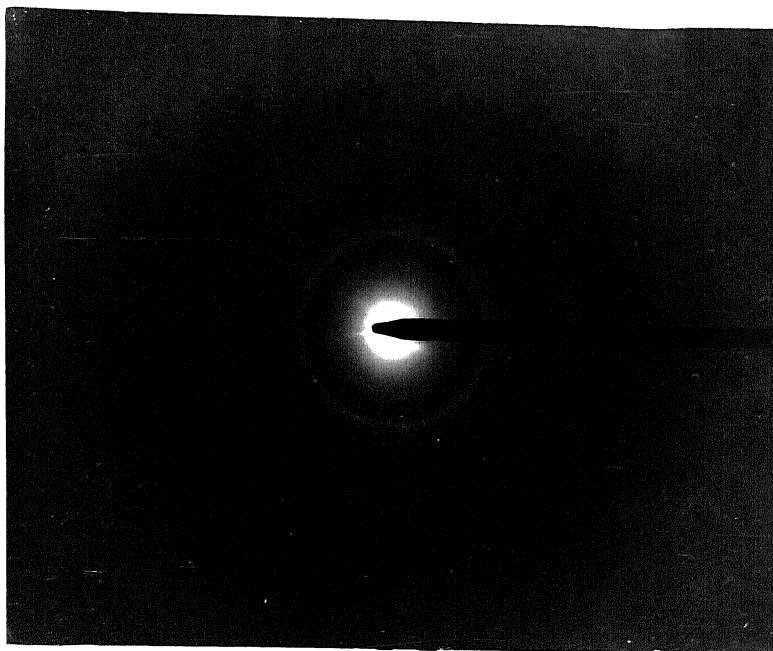


Fig.5.19 Electron diffraction pattern of a sample of glass no.5 reduced at 300°C for 1.5 hours



Fig.5.20 Electron diffraction pattern of a sample of glass no.6

Table 5.3 Comparison of calculated  $d_{hkl}$  values of glass no.2 with standard  $d_{hkl}$  values

Calculated $d_{hkl}$ $\text{\AA}$	Standard $d_{hkl}$ for bismuth <sup>108</sup> $\text{\AA}$
2.20	2.27
1.86	1.87
1.31	1.33
1.11	1.12
0.83	-

Table 5.4 Comparison of calculated  $d_{hkl}$  values of glass no.3 reduced at 200°C for 2.0 hours with standard  $d_{hkl}$  values

Calculated $d_{hkl}$ $\text{\AA}$	Standard $d_{hkl}$ for bismuth <sup>108</sup> $\text{\AA}$
2.17	2.27
1.84	1.87
1.30	1.33
1.10	1.10
0.81	-

Table 5.5 Comparison of calculated  $d_{hkl}$  values of glass no.5 reduced at 300°C for 1.5 hours with standard  $d_{hkl}$  values

Calculated $d_{hkl}$ Å	Standard $d_{hkl}$ for bismuth <sup>108</sup> Å
2.20	2.27
1.86	1.87
1.33	1.33
1.12	1.12

Table 5.6 Comparison of calculated  $d_{hkl}$  values of glass no.6 with standard  $d_{hkl}$  values

Calculated $d_{hkl}$ Å	Standard $d_{hkl}$ for bismuth <sup>108</sup> Å
2.20	2.27
1.89	1.87
1.33	1.33
1.12	1.12

### 5.4.1 Mie Theory

Mie equations<sup>137</sup> have been derived by applying Maxwell's electromagnetic equations to small conducting particles which absorb and scatter light, the dimensions of the particles being smaller than the wavelength of the optical radiation. For identical spherical particles the solution of electromagnetic equations for each particle is given by<sup>138</sup>

$$Q_{\text{scat}} = \text{Real part of } \frac{8}{3} A^4 \left[ \frac{m^2 - 1}{m^2 + 2} \right]^2 \quad (5.7)$$

$$Q_{\text{abs}} = \text{Imaginary part of } 4A \left( \frac{m^2 - 1}{m^2 + 2} \right) + \frac{4}{15} A^3 \left[ \frac{m^2 - 1}{m^2 + 2} \right]^2 \cdot \left[ \frac{m^4 + 27m^2 + 38}{2m^2 + 3} \right] \quad (5.8)$$

$$\text{where } A = \frac{2\pi r N_g}{\lambda}, \quad (5.9)$$

$r$  being the radius of particles,  $N_g$  the refractive index of glass and  $\lambda$  the wavelength.

$$m = \frac{N - iK}{N_g} \quad (5.10)$$

with  $N$  and  $K$  being the real and imaginary parts of optical constants of the particles.  $Q_{\text{scat}}$  and  $Q_{\text{abs}}$  are respectively defined as the proportions of light being scattered and absorbed by each particle divided by the cross-sectional area ( $\pi r^2$ ).

The optical density can be related by the following expression,

$$OD = \frac{3}{4} \frac{ML' Q_{ext}(2.303)}{r \rho} \quad (5.11)$$

where  $Q_{ext} = Q_{scat} + Q_{abs}$ .  $M$  is the weight fraction of the metal particles per unit volume of the composite,  $\rho$  is the density of the metallic particles and  $L'$  is the sample thickness. Since  $Q_{scat}$  is related to the 4th power of radius of particle and the primary term of  $Q_{abs}$  is linearly dependent on the particle radius for sufficiently small particle radii (around 20 nm) the contribution of  $Q_{abs}$  will be dominant. In this small particle size range, as can be seen from equations (5.9) and (5.11) the optical density is independent of particle size. On the other hand the contribution from  $Q_{scat}$  becomes significant when the particle size increases. Hence for large values of particle radii the OD is dependent on the particle size. In the latter case it is likely that the particles will deviate from spherical shape. Mie theory has been modified by Gans<sup>139,140</sup> to take into account the effect of deviation from sphericity.

#### 5.4.2 Effective medium theories

Effective medium theories have been used quite extensively to metal-dielectric microparticulate systems as we have discussed in Section 5.1.

The simplest effective medium theory is the one which has been developed by Maxwell-Garnett<sup>141</sup>. The effective permeability has been derived on the assumptions that particles are identical

spheres, they are sufficiently separated from each other to ensure independent scattering and the Lorentz correction is applicable. Under these assumptions the effective permeability ( $\bar{\epsilon}^{MG}$ ) is given by,

$$\frac{\bar{\epsilon}^{MG} - \epsilon_m}{\bar{\epsilon}^{MG} + 2\epsilon_m} = f \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \quad (5.12)$$

where  $\epsilon_m$  is the dielectric permittivity of the matrix,  $f$  the fill factor and  $\epsilon$  the permittivity of an individual particle.

It has been shown by Onsager<sup>142</sup> that only part of the field is effective in directing the dipoles in a dielectric matrix. Polder and van Santen<sup>143</sup> have incorporated Onsager's 'reaction field' to derive an improved effective medium permeability for particles of ellipsoidal shapes. Combining their calculations with MG approach the following effective medium permeability ( $\bar{\epsilon}^{MG-PvS}$ ) can be obtained<sup>122</sup>

$$\bar{\epsilon}^{MG-PvS} = \epsilon_m \frac{1 + \frac{2}{3} \sum_j f_j \delta_j}{1 - \frac{1}{3} \sum_j f_j \delta_j} \quad (5.13)$$

where  $f_j$  is the fill factor of the particles belonging to the  $j$ th class, such that  $\sum_j f_j = f$ , where  $f$  is the fill factor.  $\delta_j$  is related to the polarisability of the particles in  $j$ th interval and for ellipsoidal shape is given by<sup>122</sup>

$$\delta_j = \frac{1}{3} \sum_{k=1}^3 \frac{\epsilon_j - \bar{\epsilon}}{\bar{\epsilon} + L_k(\epsilon_j - \bar{\epsilon})} \quad (5.14)$$



where  $\epsilon_j$  is the size dependent dielectric permittivity of the particle.  $\bar{\epsilon}$  is the effective permeability which can be calculated from any effective medium theory.  $L_k$ 's are the triplet of depolarisation factors. It can be seen that for equal-sized spheres with  $L_1 = L_2 = L_3 = 1/3$ , the equation (5.13) reduces to the Maxwell-Garnett expression (5.12). Both MG and MG-PvS theories are applicable for small values of the fill factor.

Another effective medium theory has been put forward by Bruggeman<sup>144</sup>. In this a particle is considered to be embedded in an effective medium and its properties are determined self-consistently. To achieve this one has to solve for local field around the particles such that the fluctuations average out to zero. From these requirements the effective medium permeability ( $\bar{\epsilon}^{BR}$ ) is given by,

$$\bar{\epsilon}^{BR} = \epsilon_m \frac{1 - f + \frac{1}{3} \sum_j f_j \delta_j}{1 - f - \frac{2}{3} \sum_j f_j \delta_j} \quad (5.15)$$

where  $\delta_j$  is given by the expression (5.14). In principle this theory is applicable to any fill factor, as it gives equal weightage to the components of the inhomogeneous medium.

Hunderi<sup>145</sup> has derived an expression for the effective permeability  $\bar{\epsilon}^{HU}$  from the back scattered field and it is given by,

$$\frac{-\mathbf{H}\mathbf{U}}{\epsilon} = \epsilon_m \left( \frac{1 + \frac{1}{4} \sum_j f_j \delta_j}{1 - \frac{1}{4} \sum_j f_j \delta_j} \right)^2 \quad (5.16)$$

$\delta_j$  being given by the expression (5.14). The theory is applicable for small fill factor.

Recently both MG and BR theories have been derived by Niklasson et al.<sup>146</sup> from an unified approach by specifying two types of random unit cells which represent two types of microstructures and on the requirement that these cells when embedded in an effective medium will not be detected by an electromagnetic wave.

In the small particle size range, the grain boundary scattering should influence the mean free path of conduction electrons and hence the dielectric permeability will be particle size dependent. Secondly when the particles are not far apart the dipole-dipole interaction cannot be neglected. This interaction can be included by replacing the  $\delta_j$ 's in equation (5.14) by a set of equivalent depolarisation factors defined for different geometrical configurations of identical spheres<sup>122</sup>.

#### 5.4.3 Validity of effective medium formalism

The criterion for the validity of effective medium model as examined by Granqvist<sup>122</sup> is that the results predicted should be independent of experimental condition used. When a plane wave with an amplitude  $U_0$  is incident on a thick slab

containing independently scattering particles the back scattered field has been given by Van de Hulst<sup>147</sup> as  $i\pi U_0 \rho_p S(\pi)/k^3$  where  $\rho_p$  is the particle number density,  $S(\pi)$  the scattering amplitude function at an angle  $\pi$  and  $k$  is the wave vector. The refractive index of the medium corresponding to this field is given by<sup>145</sup>,

$$N_R \simeq 1 - i2\pi \rho_p S(\pi)/k^3 \quad (5.17)$$

In the transmission measurement the refractive index is given by<sup>147</sup>,

$$N_T \simeq 1 - i2\pi \rho_p S(0)/k^3 \quad (5.18)$$

The ratio of  $S(\pi)/S(0)$  as calculated by Van de Hulst<sup>147</sup> from the Mie theory is given by,

$$S(\pi)/S(0) = 1 + \frac{k^2 x^2}{15} \left[ \frac{(\epsilon+4)(\epsilon+2)}{2\epsilon+3} \right] + O(k^4 x^4) \quad (5.19)$$

where  $\epsilon$  is the dielectric permittivity of the particles. In order for the effective medium approach to be valid, therefore,  $N_R$  and  $N_T$  should not differ appreciably from each other. This means that  $S(\pi)/S(0)$  should be around 1. For the real and imaginary parts of the second term of equation (5.19) to be smaller than around 5 percent, the particle size will be of the order of 10 nm or less for gold<sup>122</sup>. The 3rd row of table 5.2 shows that the particle size is of the same order of magnitude in the present investigation. Therefore in the following

sections we have used effective medium theories to interpret the optical absorption data as reported in Section 5.3.

### 5.5 Interpretation of Experimental Results

From tables 5.3 to 5.6 we see that the calculated  $d_{hkl}$  values compare well with the standard  $d_{hkl}$  values of metallic bismuth. The SAD data thus confirm that the particles observed in the different glass matrices consist of metallic bismuth.

#### 5.5.1 Computation procedure

The frequency dependent dielectric permittivity of bismuth is of prime importance in interpreting the optical absorption data by effective medium theories. To start with the frequency dependent bulk dielectric permittivity of bismuth has been calculated from the index of refraction and extinction coefficient given as a function of wavelength in reference ([148]). The size dependent dielectric permittivity of bismuth has been obtained from the bulk data by incorporating the size dependent electron scattering in the Drude free electron part of the dielectric permittivity as follows<sup>122</sup>

$$\epsilon_j(\omega) = \epsilon_{\text{exp}}(\omega) - \epsilon_{\text{exp}}^{\text{Drude}}(\omega) + \epsilon_j^{\text{Drude}}(\omega) \quad (5.19a)$$

where  $\omega$  is the angular frequency of radiation used. The last two terms in the right hand side of the above equation are given by,

$$\epsilon_{\text{exp}}^{\text{Drude}}(\omega) = 1 - \omega_{\text{pb}}^2 / \omega(\omega + i/\tau_b) \quad (5.20)$$

$$\epsilon_j^{\text{Drude}}(\omega) = 1 - \omega_{\text{px}_j}^2 / \omega(\omega + i/\tau_j) \quad (5.21)$$

where  $\omega_{\text{pb}}$  and  $\tau_b$  are the bulk plasma frequency and the mean electron life time respectively.  $\omega_{\text{px}_j}$  is the apparent plasma frequency of particle of size  $x_j$  and  $\tau_j$  is given by,

$$\tau_j^{-1} = \tau_b^{-1} + 2v_{\text{Fb}}/x_j \quad (5.22)$$

where  $v_{\text{Fb}}$  is the bulk Fermi velocity of electrons and  $x_j$  the particle size of the  $j$ th class. A value of  $\hbar\omega_{\text{pb}} = 16.0$  eV has been taken from reference ([149]). Values of  $\tau_b/\hbar = 2.838$  eV and  $v_{\text{Fb}} = 1.822 \times 10^8$  cm/sec. have been calculated using free electron model<sup>150</sup>.

Separating the real and imaginary parts of the size dependent dielectric permittivity ( $\epsilon_j = \epsilon_j' + i\epsilon_j''$ ) from equations (5.19a) to (5.21) we get after simplification,

$$\epsilon_j'(\omega) = \epsilon_{\text{exp}}'(\omega) + \frac{\omega_{\text{pb}}^2}{\omega^2 + 1/\tau_b^2} - \frac{\omega_{\text{px}_j}^2}{\omega^2 + [(x_j + 2\tau_b v_{\text{Fb}})/\tau_b x_j]^2} \quad (5.23)$$

$$\epsilon_j''(\omega) = \epsilon_{\text{exp}}''(\omega) + \frac{\omega_{\text{px}_j}^2 [(x_j + 2\tau_b v_{\text{Fb}})/\tau_b x_j]}{\omega [\omega^2 + \{(x_j + 2\tau_b v_{\text{Fb}})/\tau_b x_j\}^2]} - \frac{\omega_{\text{pb}}^2 / \tau_b \omega}{\omega^2 + (1/\tau_b^2)} \quad (5.24)$$

### 5.5.1.1 MG effective medium theory

Simplifying equation (5.12) and then separating the real and imaginary parts of  $\bar{\epsilon}^{MG}$  ( $\bar{\epsilon}^{MG} = \bar{\epsilon}_1^{MG} + i\bar{\epsilon}_2^{MG}$ ) we get,

$$\bar{\epsilon}_1^{MG} = \frac{AC + BD}{C^2 + D^2} \quad (5.25)$$

$$\bar{\epsilon}_2^{MG} = \frac{BC - AD}{C^2 + D^2} \quad (5.26)$$

where,

$$A = \epsilon_m(1+2f)\epsilon' + 2\epsilon_m^2(1-f) \quad (5.27a)$$

$$B = \epsilon_m(1+2f)\epsilon'' \quad (5.27b)$$

$$C = (1-f)\epsilon' + \epsilon_m(2+f) \quad (5.27c)$$

$$D = (1-f)\epsilon'' \quad (5.27d)$$

In equations(5.27),  $\epsilon'$  and  $\epsilon''$  are given by equations (5.23) and (5.24) respectively in which  $x_j$  is replaced by the average particle size as computed by equation (5.1). The frequency dependent  $\bar{\epsilon}_1^{MG}$  and  $\bar{\epsilon}_2^{MG}$  have been computed using equations (5.25) to (5.27). For bismuth in silicate and in  $V_2O_5-P_2O_5$  systems the dielectric permittivity of the media are taken as 2.2<sup>[128]</sup> and 10<sup>[151]</sup> respectively.

### 5.5.1.2 MG-PvS and BR theories

Equations (5.13) and (5.15) contain size dependent fill factor which can be related to  $f$  by the following equation,

$$f_j = w_j f \quad (5.28)$$

where  $w_j$  is the weight factor and is given by,

$$w_j = \frac{x_j^3 n_j}{\sum_j x_j^3 n_j} \quad (5.29)$$

where  $n_j$  is the number of particles in  $j$ th class.

From equation (5.13) separating the real and imaginary parts of the complex quantities, we get the real and imaginary parts of the effective medium permeability in the MG-PvS theory as follows :

$$\bar{\epsilon}_1 = \epsilon_m \frac{A_1 C_1 - B_1 D_1}{C_1^2 + D_1^2} \quad (5.30)$$

$$\bar{\epsilon}_2 = \epsilon_m \frac{B_1 C_1 + A_1 D_1}{C_1^2 + D_1^2} \quad (5.31)$$

where,

$$A_1 = 1 + \frac{2}{3} f \sum_j w_j \delta_j' \quad (5.32a)$$

$$B_1 = \frac{2}{3} f \sum_j w_j \delta_j'' \quad (5.32b)$$

$$C_1 = 1 - \frac{1}{3} f \sum_j w_j \delta_j' \quad (5.32c)$$

$$D_1 = \frac{1}{3} f \sum_j w_j \delta_j'' \quad (5.32d)$$

$\delta_j'$  and  $\delta_j''$  of the above equations (5.32) are given by,

$$\delta_j' = \frac{1}{3} \sum_{k=1}^3 \frac{EG_k + FH_k}{G_k^2 + H_k^2} \quad (5.33)$$

$$\delta_j'' = \frac{1}{3} \sum_{k=1}^3 \frac{FG_k - EH_k}{G_k^2 + H_k^2} \quad (5.34)$$

where,

$$E = \epsilon_j' - \bar{\epsilon}_1 \quad (5.35a)$$

$$F = \epsilon_j'' - \bar{\epsilon}_2 \quad (5.35b)$$

$$G_k = L_k \epsilon_j' + (1-L_k) \bar{\epsilon}_1 \quad (5.35c)$$

$$H_k = L_k \epsilon_j'' + (1-L_k) \bar{\epsilon}_2 \quad (5.35d)$$

In the above equations  $\epsilon_j'$  and  $\epsilon_j''$  are given by expressions (5.23) and (5.24) respectively. In the Bruggeman formalism, the expressions (5.30) to (5.35) will be identical with  $A_1, B_1, C_1$  and  $D_1$  of equations (5.32(a) to 5.32(d)) being properly replaced by using the Bruggeman effective medium equation (5.15).

In order to compute the value of  $\bar{\epsilon}_1$  and  $\bar{\epsilon}_2$  from equations (5.30) and (5.31), we notice that the equations are of the transcendental type as they involve  $\bar{\epsilon}_1$  and  $\bar{\epsilon}_2$  on the right hand side through  $\delta_j'$  and  $\delta_j''$  respectively. So  $\bar{\epsilon}_1$  and  $\bar{\epsilon}_2$  have been found iteratively as follows. First  $\bar{\epsilon}_1$  in the right hand side is assigned the value of  $\epsilon_m$  and we set  $\bar{\epsilon}_2 = 0$ . Then  $\bar{\epsilon}_1$  and  $\bar{\epsilon}_2$  are calculated from the equations (5.30) and (5.31).  $\bar{\epsilon}_1$  and  $\bar{\epsilon}_2$  of the right hand side of equations (5.30) and (5.31) are replaced by the new values as calculated in the previous iteration and  $\bar{\epsilon}_1$  and  $\bar{\epsilon}_2$  are calculated from equations (5.30)



and (5.31). This process is continued until the difference between two successive iterations is less than a preassigned error. In our calculation we have used an error of 0.1.  $L_k$ 's, the depolarisation factors for sphere are taken from the reference ([122]). Once the frequency dependent  $\bar{\epsilon}_1$  and  $\bar{\epsilon}_2$  are computed, the optical absorption coefficient ( $\alpha$ ) is then given by,

$$\alpha(\omega) = (\omega/c)(\bar{\epsilon}_2/\bar{\epsilon}_1^{\frac{1}{2}}) \quad (5.36)$$

The frequency dependent  $\alpha$  values as computed as a function of wavelength  $\lambda$  from MG, MG-PvS and BR theories for the  $V_2O_5$ - $P_2O_5$  and silicate systems under investigation are plotted in figures 5.21 to 5.32. In each figure is included the corresponding experimentally determined  $\alpha$  values for comparison. Table 5.7 contains the theoretical and experimental  $\alpha$  values corresponding to peak positions. It is observed that computed  $\alpha$  values by BR and MG-PvS theories are almost identical as are evident from figures 5.21 to 5.32. So in table 5.7 we have only included  $\alpha$  values computed by MG and BR theories. The theoretically computed  $\alpha$  values for vanadium phosphate glasses containing bismuth show a small absorption peak at 650 nm while in the case of silicate glasses containing bismuth the calculated  $\alpha$  values show a small dip. However, no peak is observed experimentally in either of these systems around this wavelength.

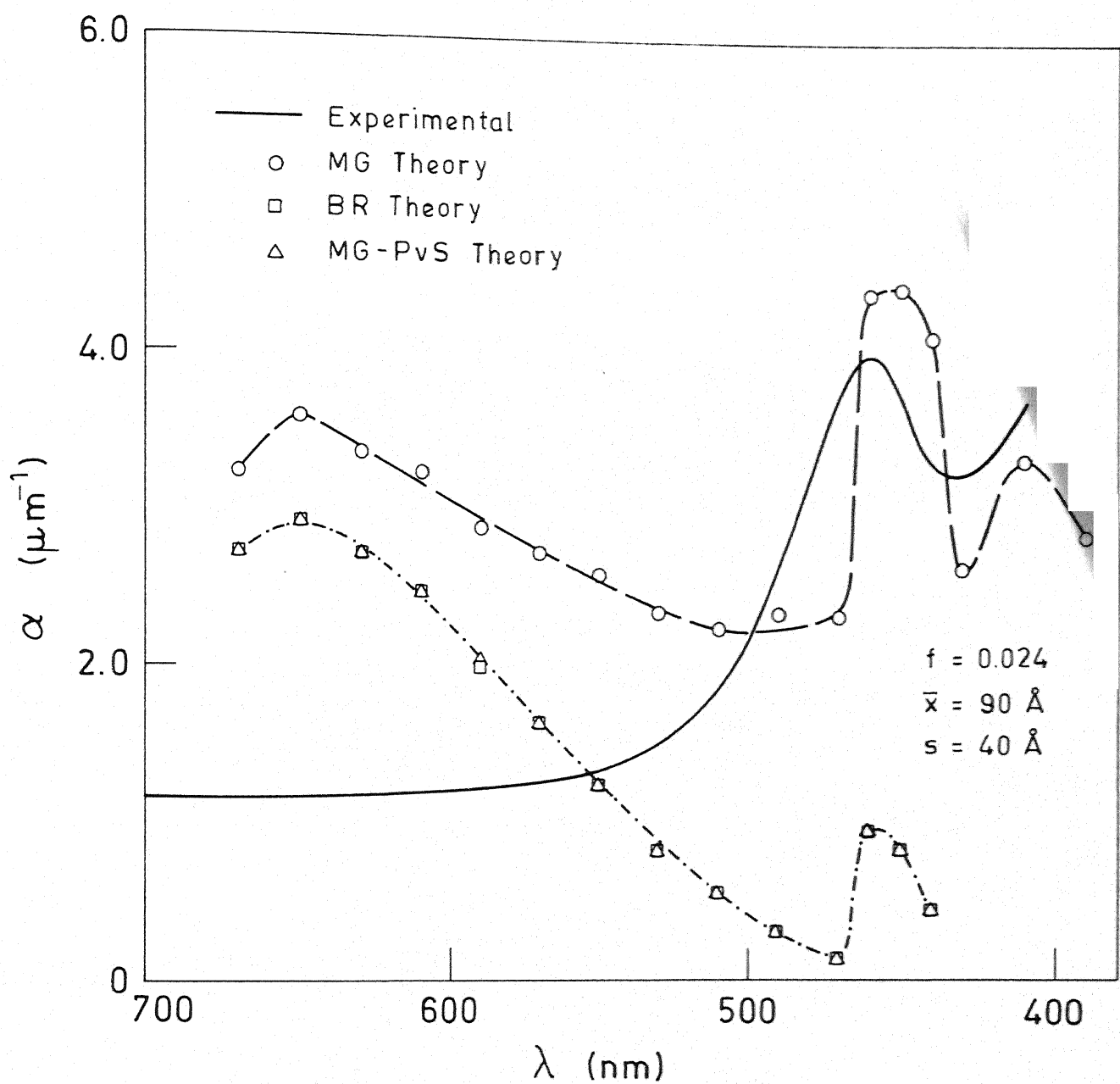


Fig. 5.21 Comparison of experimental and theoretical absorption coefficient  $\alpha$  for glass no. 2.

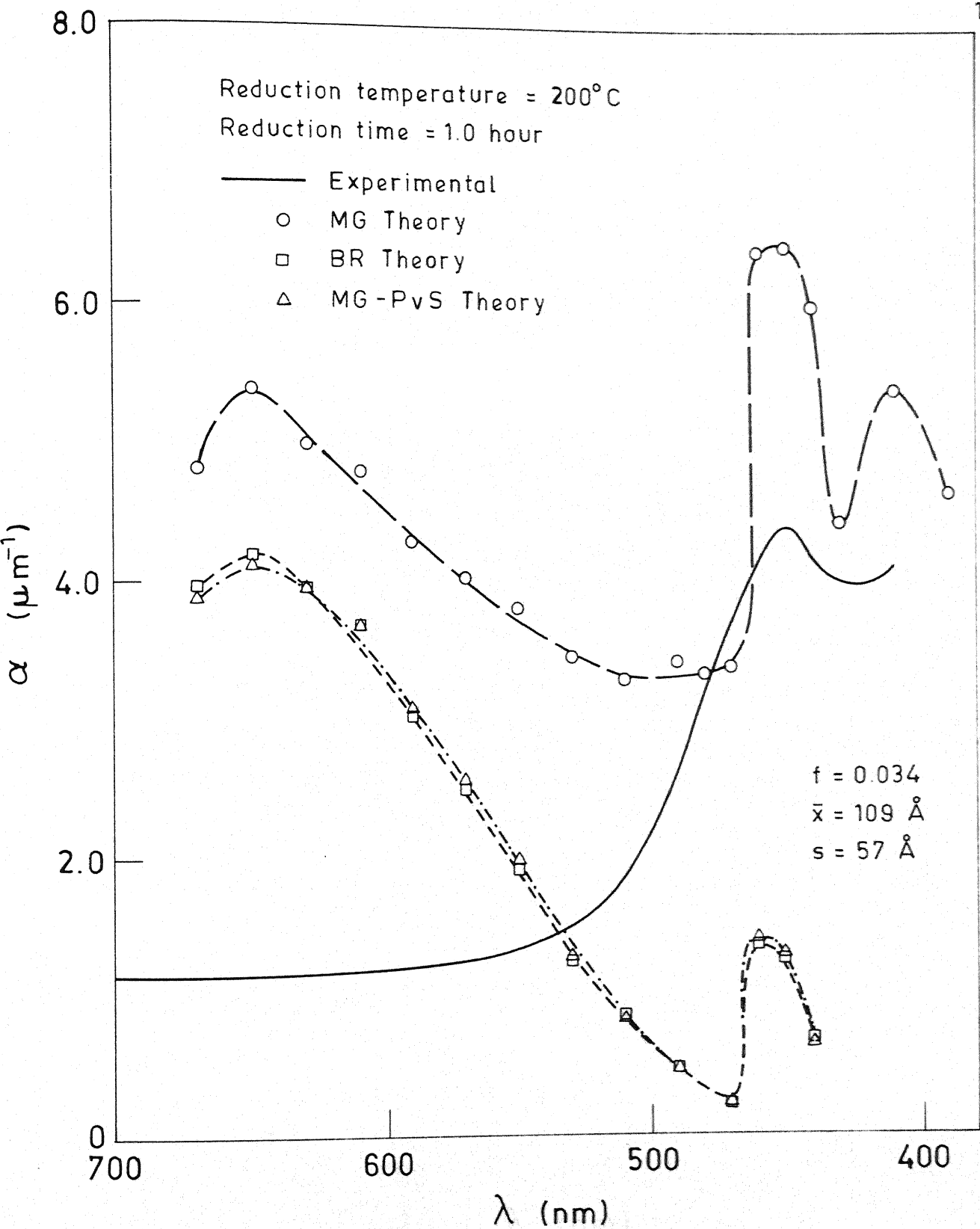


Fig. 5.22 Comparison of experimental and theoretical absorption coefficient  $\alpha$  for glass no. 2.

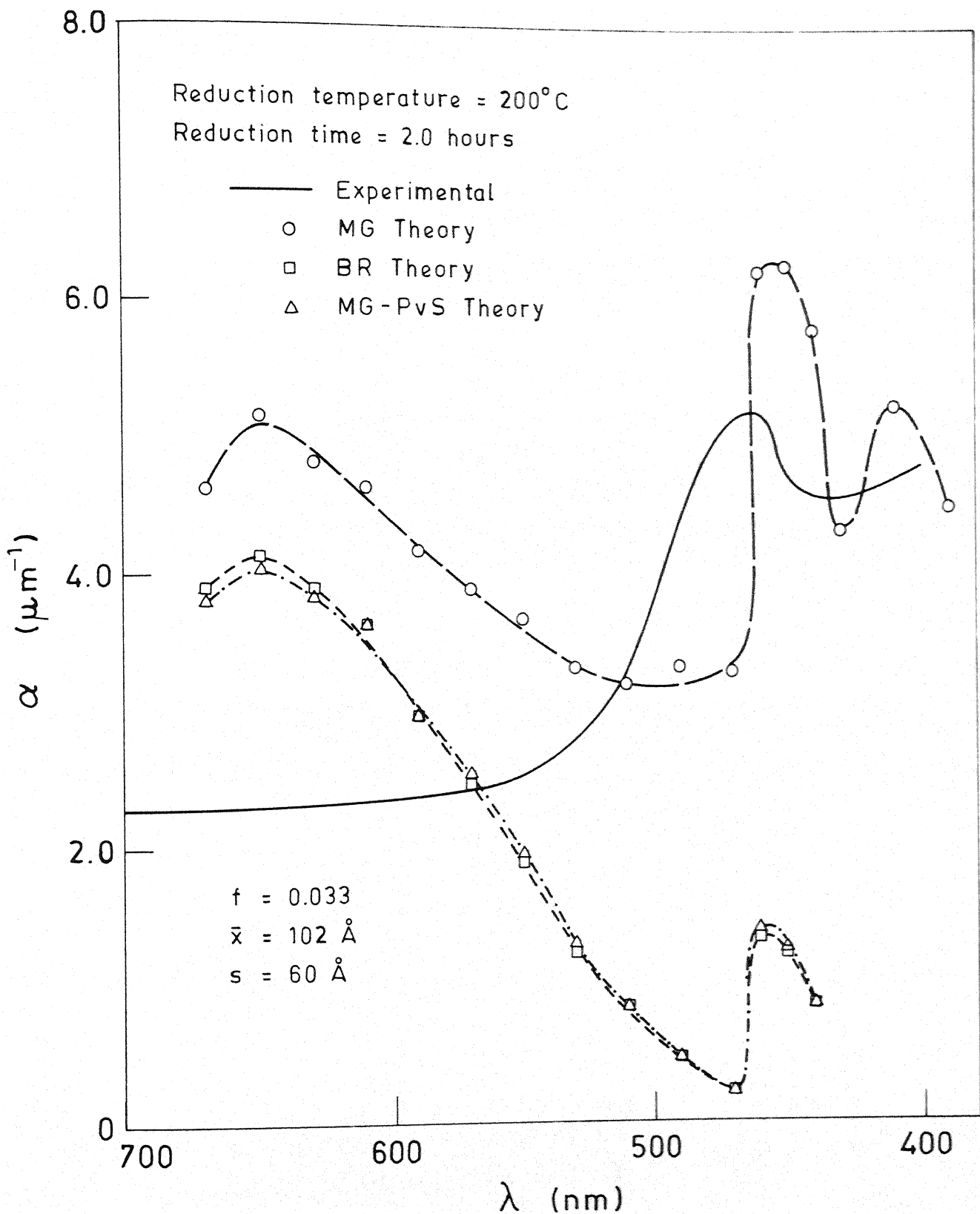


Fig. 5.23 Comparison of experimental and theoretical absorption coefficient  $\alpha$  for glass no. 2.

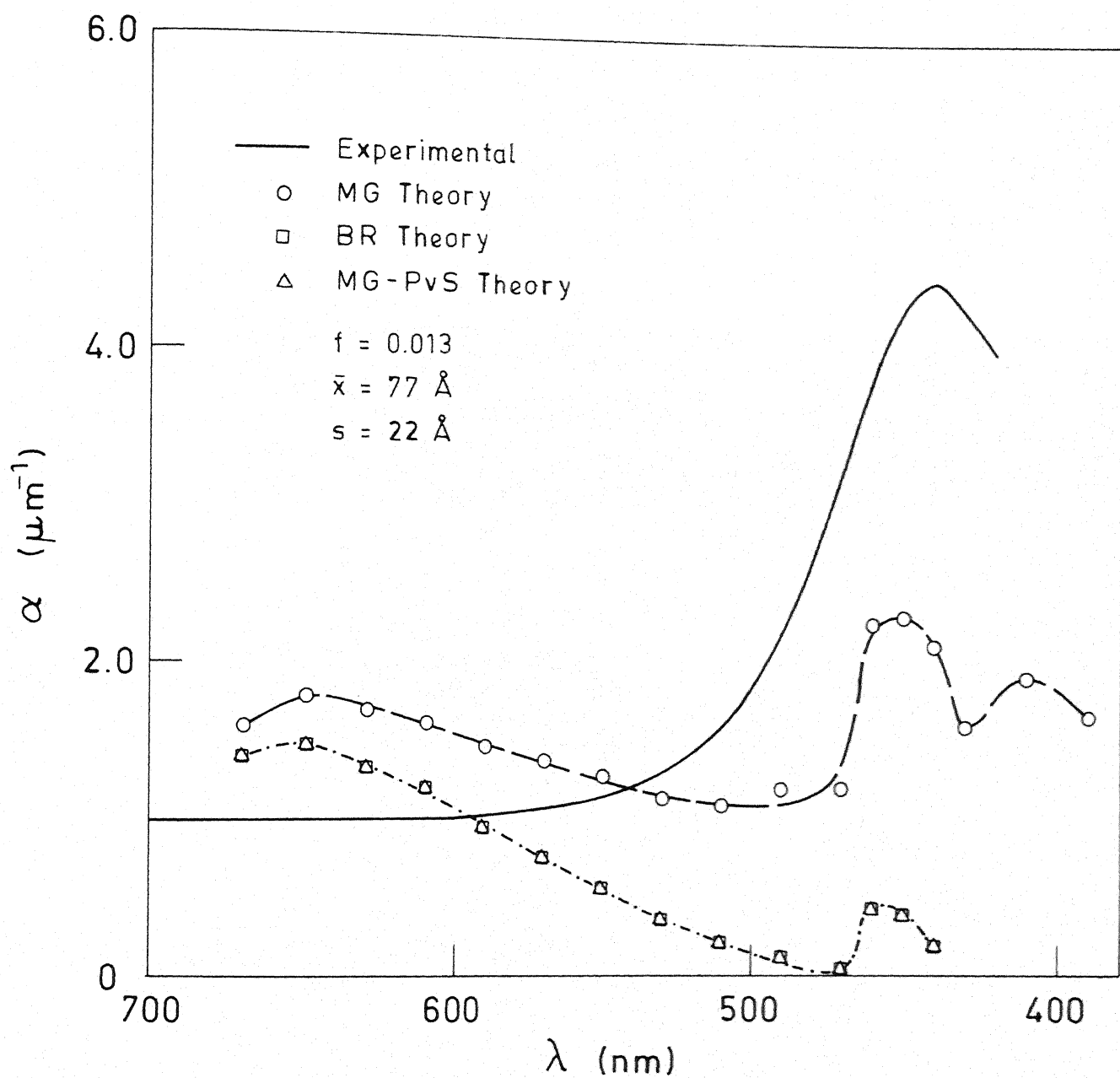


Fig. 5.24 Comparison of experimental and theoretical absorption coefficient  $\alpha$  for glass no. 3.

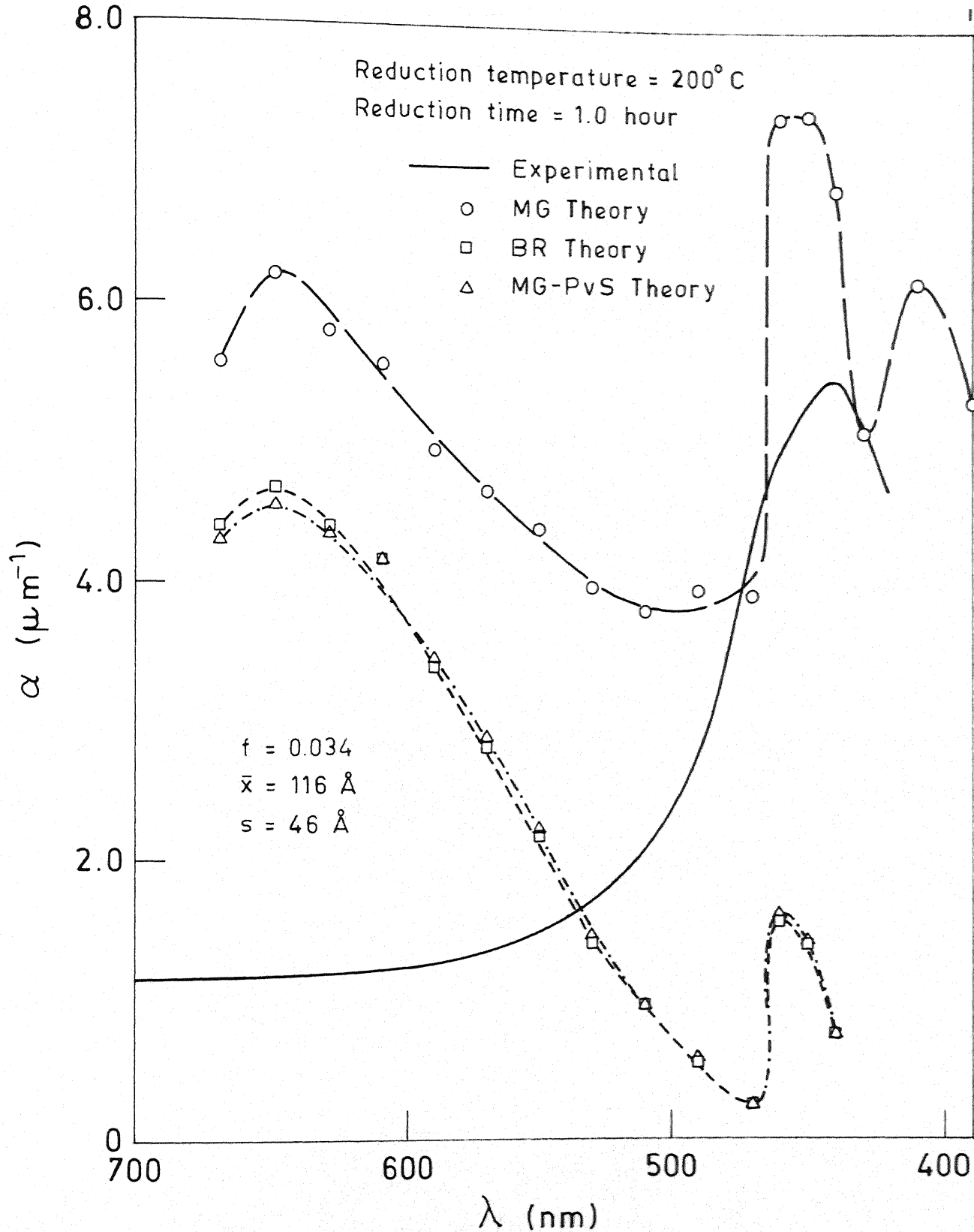


Fig. 5.25 Comparison of experimental and theoretical absorption coefficient  $\alpha$  for glass no. 3.

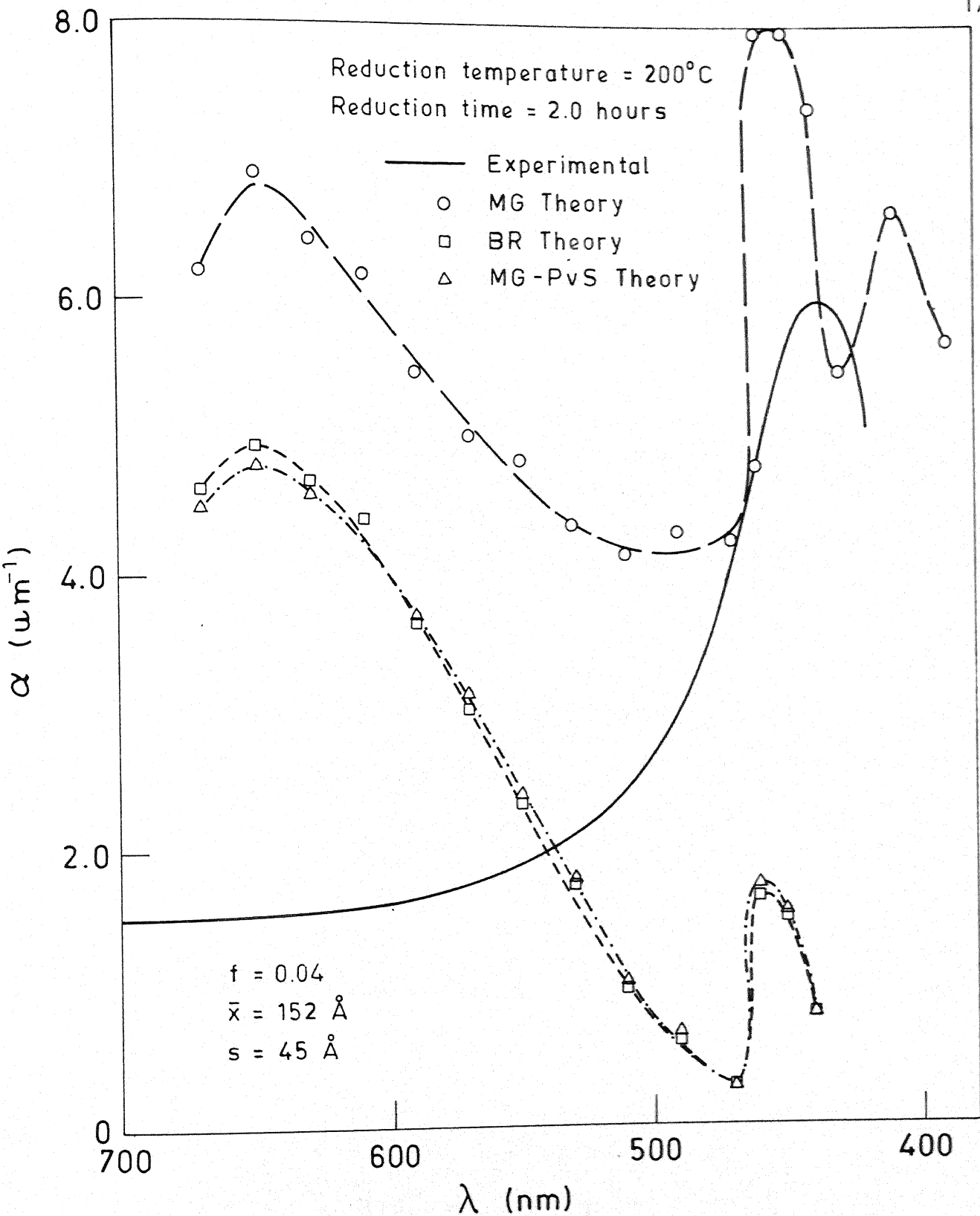


Fig. 5.26 Comparison of experimental and theoretical absorption coefficient  $\alpha$  for glass no. 3.

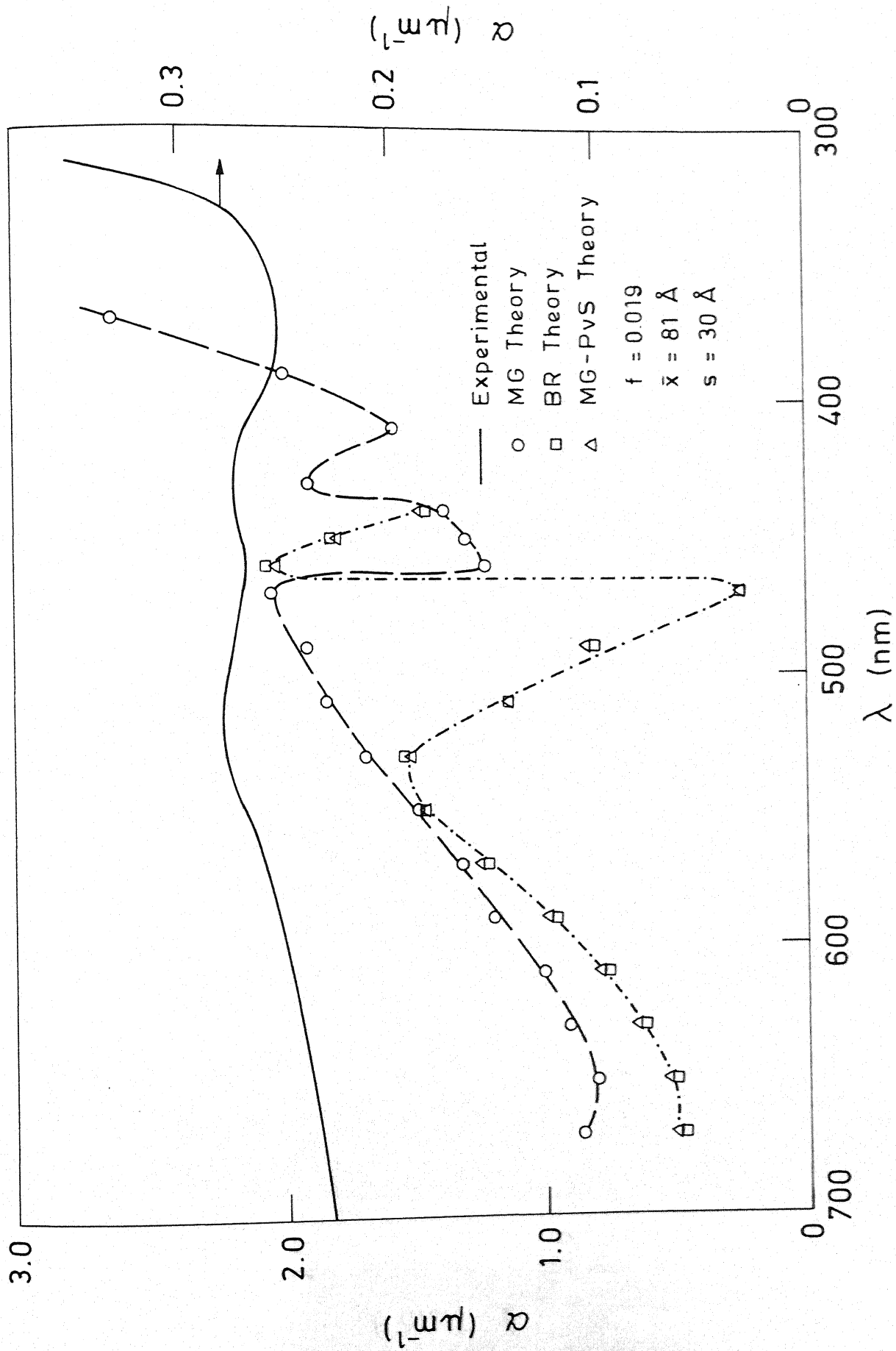


Fig. 5.27 Comparison of experimental and theoretical absorption coefficient  $\alpha$  for glass no. 5.



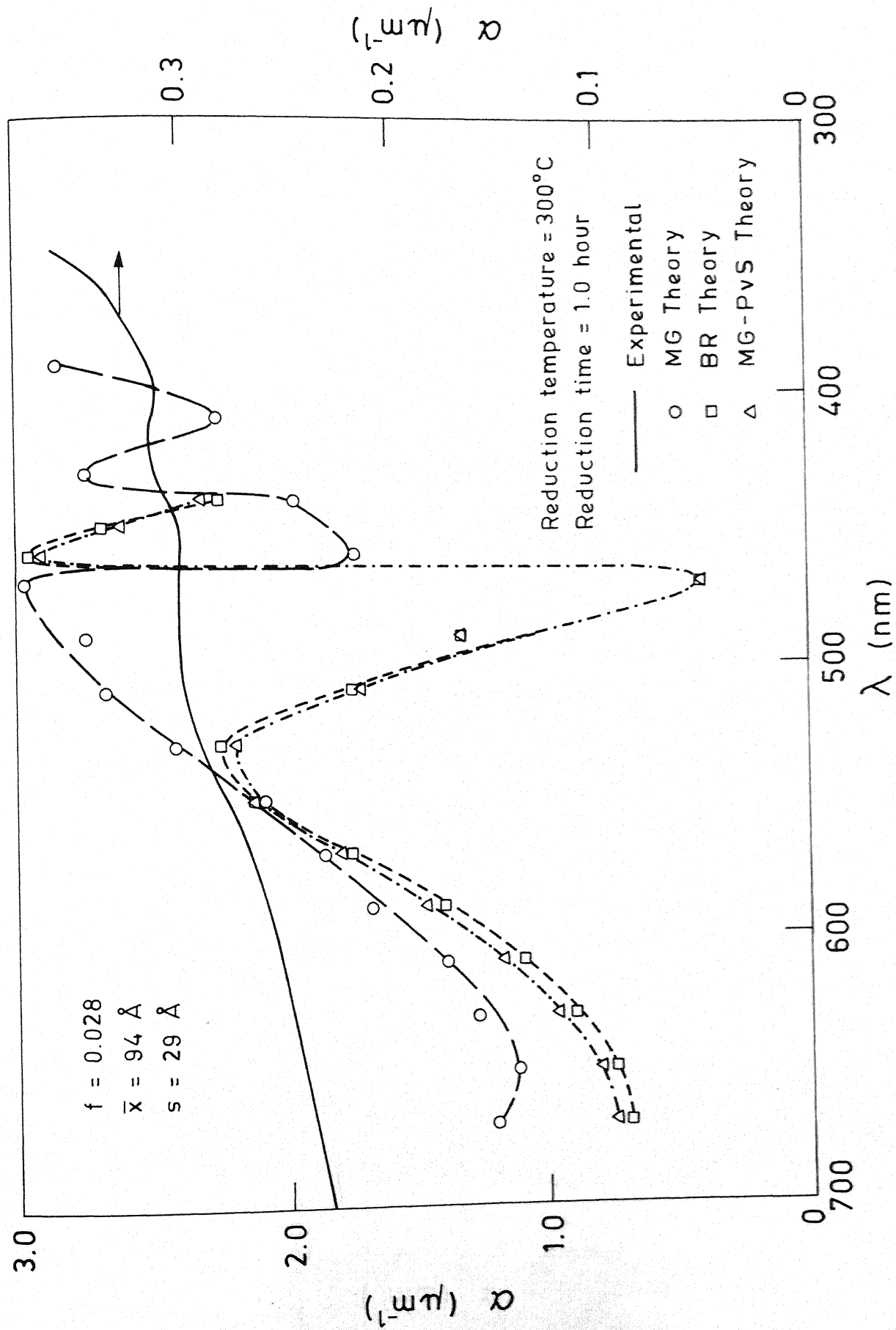


Fig. 5.28 Comparison of experimental and theoretical absorption coefficient  $\alpha$

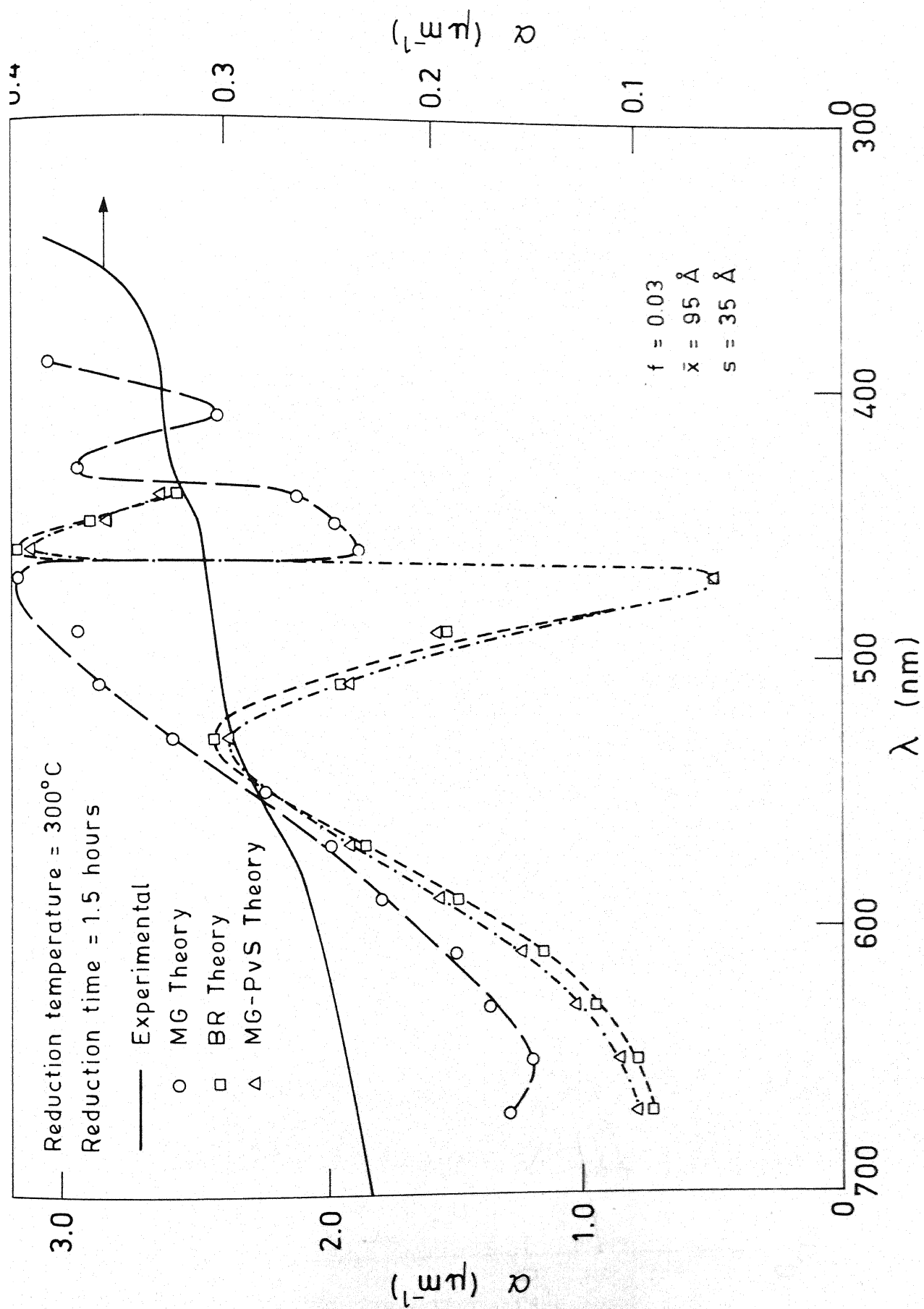


Fig. 5.29 Comparison of experimental and theoretical absorption

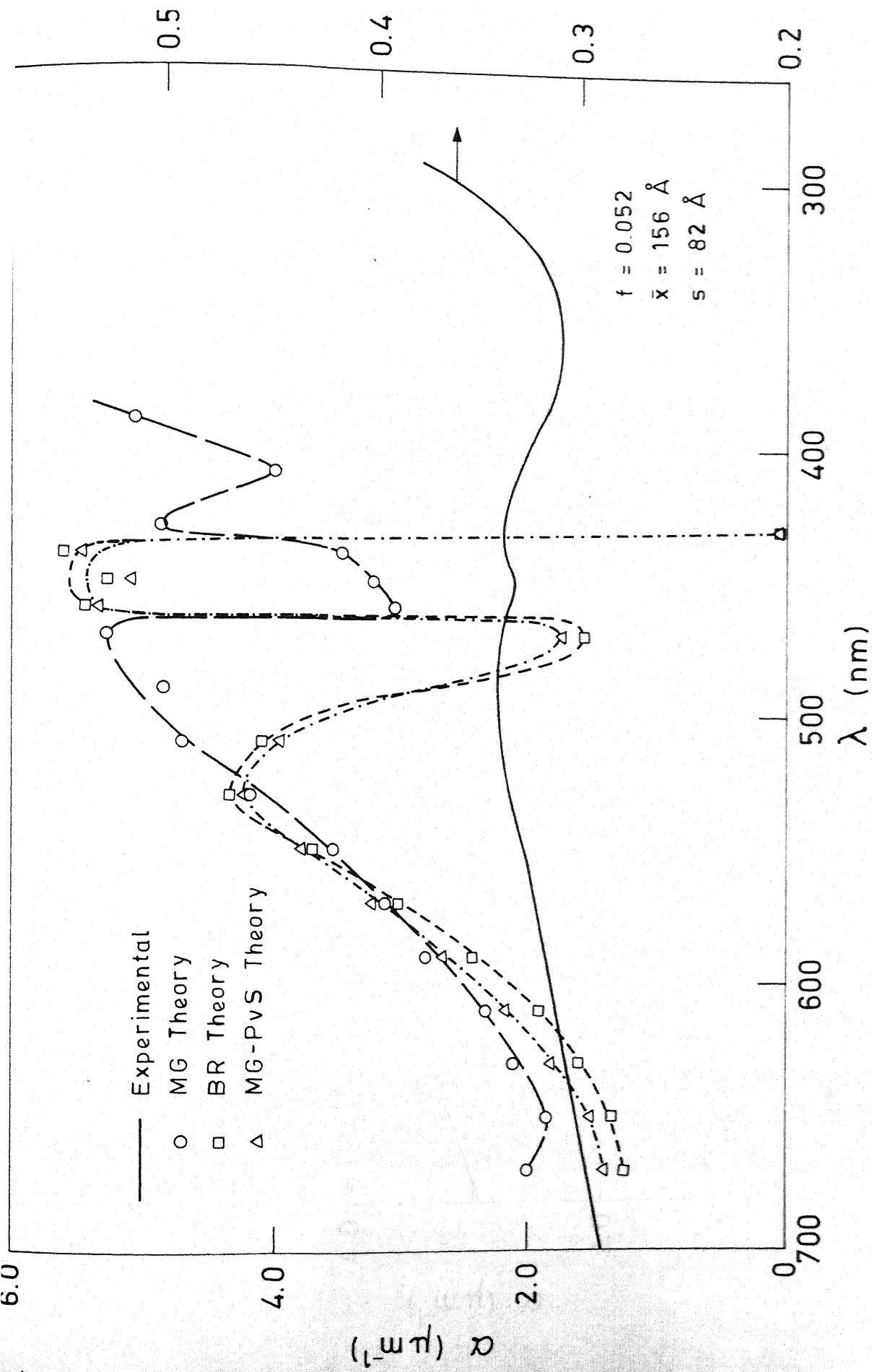


Fig. 5.30 Comparison of experimental and theoretical absorption coefficient  $\alpha$  for glass no. 6.

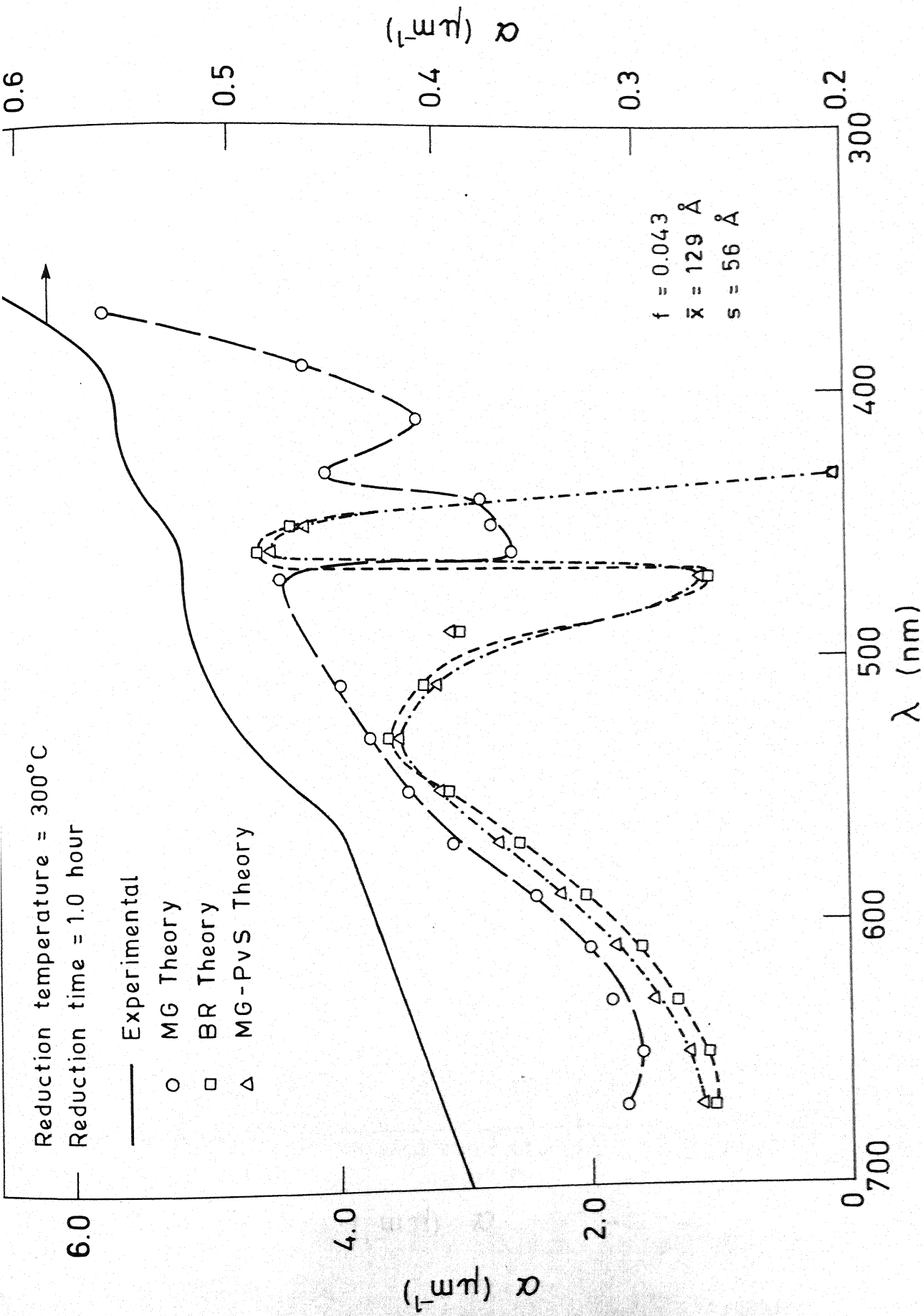


Fig. 5.31 Comparison of experimental and theoretical absorption

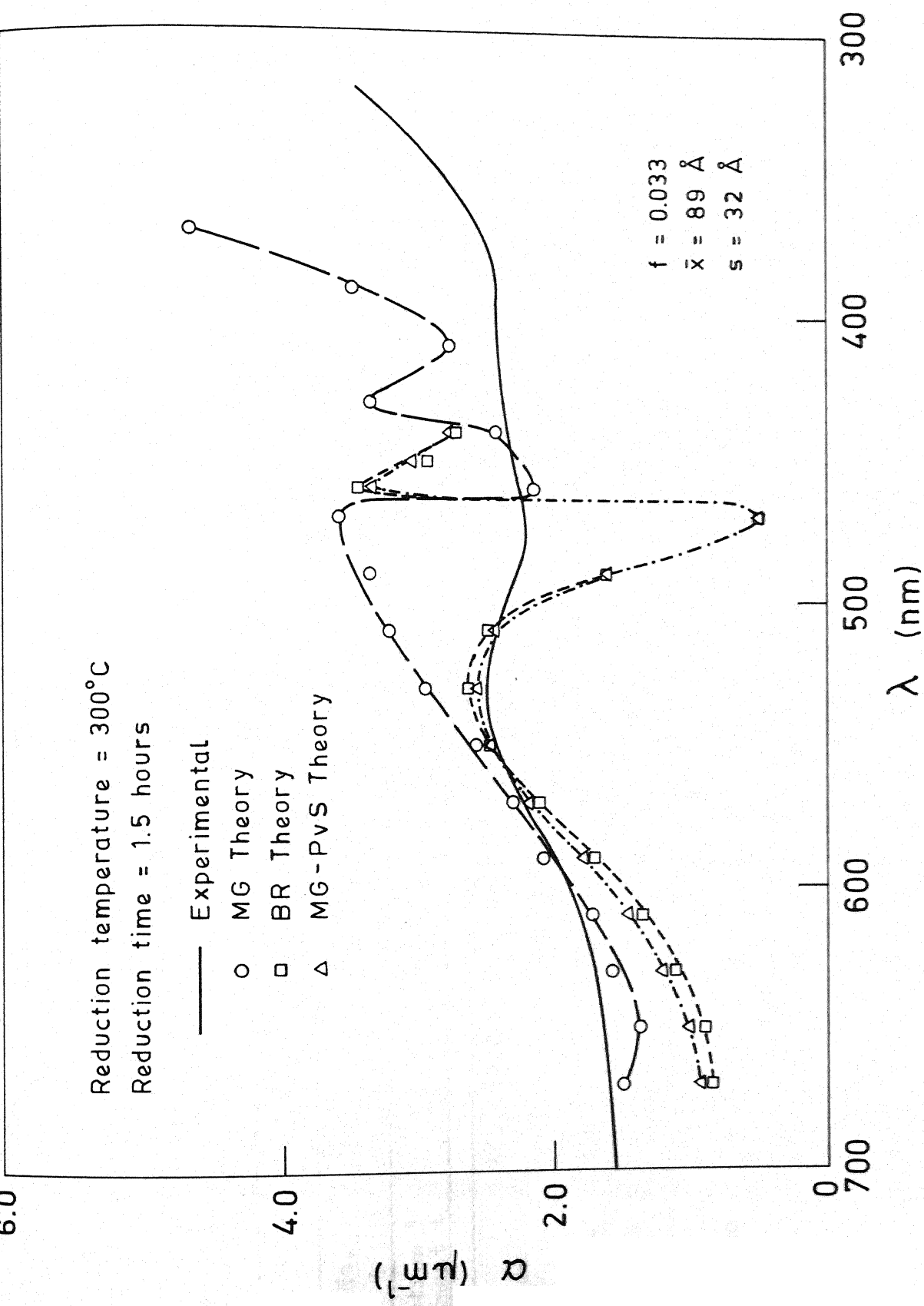


Fig. 5.32 Comparison of experimental and theoretical absorption coefficient  $\alpha$  for glass no. 6.

Table 5.7 Comparison of experimental and theoretical  $\alpha$  values for different glasses

Glass System	$V_2O_5-P_2O_5-Bi_2O_3$				$SiO_2-B_2O_3-Na_2O-Bi_2O_3$			
Glass No.	2				5			
	3				6			
Reduction T	200	200	200	200	300	300	300	300
Treatment t	1	2	1	2	1	1.5	1	1.5
	Experimental							
Peak position nm(1)	460	450	460	440	440	520	500	500
Peak value $\alpha \mu m^{-1}(1)$	4.0	4.4	5.2	4.48	5.6	6.0	0.28	0.303
Peak position nm(2)	-	-	-	-	-	430	420	420
Peak value $\alpha \mu m^{-1}(2)$	-	-	-	-	-	0.275	0.313	0.325
						0.34	0.34	0.515
						2.48		

contd ....

Theoretical - M G

Peak position $\alpha \mu\text{m}^{-1}(1)$	450	450	450	450	450	450	450	470	470	470	470	470
Peak value $\alpha \mu\text{m}^{-1}(1)$	4.44	6.44	6.28	2.32	7.4	8.0	2.04	2.96	3.18	5.24	4.4	3.6
Peak position $\alpha \mu\text{m}^{-1}(2)$	410	410	410	410	410	410	430	430	430	430	430	430
Peak value $\alpha \mu\text{m}^{-1}(2)$	3.32	5.44	5.24	1.92	6.2	6.6	1.9	2.74	2.94	4.84	3.68	3.36

Theoretical - B R

Peak position $\alpha \mu\text{m}^{-1}(1)$	460	460	460	460	460	460	460	530	530	530	530	530
Peak value $\alpha \mu\text{m}^{-1}(1)$	0.96	1.36	1.32	0.44	1.6	1.68	1.54	2.26	2.44	4.32	3.6	2.64
Peak position $\alpha \mu\text{m}^{-1}(2)$	-	-	-	-	-	-	460	460	460	460	460	460
Peak value $\alpha \mu\text{m}^{-1}(2)$	-	-	-	-	-	-	2.04	2.96	3.18	5.4	4.6	3.44

Note : T - Reduction temperature in degree C  
t - Reduction time in hours.

In  $V_2O_5$ - $P_2O_5$  system as the reduction time increases the experimental  $\alpha$  values at peak positions increase (2nd row of table 5.7 and figure 5.3). This is because of the fact that with increasing reduction time the amount of precipitated bismuth becomes larger. It is evident from the second row of table 5.2 that the volume fraction ( $f$ ) increases with an increase in reduction time. From the 5th and 7th rows of table 5.7 we see that  $\alpha$  values as calculated by MG theory show two peak positions at 450 nm and 410 nm while BR theory predicts one peak at 460 nm. Beyond 440 nm the values of  $\bar{\epsilon}_1$  as calculated by BR and MG-PvS theories become negative. Experimentally we could not observe the second peak as the experimental OD could not be measured because of the full opening of the slit in Carry 17D beyond about 410 nm. Comparing the 1st and 5th rows of table 5.7 we see that the first peak position as predicted by MG theory agrees with the experimentally observed value within  $\pm 10$  nm. The peak position predicted by BR theory (9th row of table 5.7) agrees with the experimental one within an error of 20 nm. MG theory predicts results which are in better agreement with experiment than those obtained from BR and MG-PvS theories. This is evident from figures 5.21 to 5.26. It is observed that calculated  $\alpha$  values by MG, BR and MG-PvS theories increase with increase in reduction time except for glass no.2 reduced at  $200^\circ\text{C}$  for 2.0 hours. From 2nd row of table 5.2 we see that  $f$



increases with increase in reduction time except for the one just mentioned. Except for this sample the theoretically observed trend of  $\alpha$  values with reduction time is in agreement with experimental results.

In the silicate system we find two broad absorption peaks. This is evident from figure 5.4. From 1st and 3rd rows of tables 5.7 we see that two absorption peaks occur in the range of 500-530 nm and 420 to 430 nm respectively. The corresponding calculated peak positions by MG theory occur at 470 nm and 430 nm respectively (5th and 7th rows of table 5.7) and those computed by BR theory occur at 530 nm and 460 nm respectively (9th and 11th rows of table 5.7). Therefore, it is clear that no effective medium theory by itself can predict the peak position accurately.

From the study of table 5.7 and also from figures 5.21 to 5.32 we find that the discrepancy between the theory and the experimental data is more in silicate system than in the  $V_2O_5$ - $P_2O_5$  system. The calculated  $\alpha$  values in the silicate system (6th, 8th, 10th and 12th rows of table 5.7) are an order of magnitude greater than those observed experimentally near the peak positions (2nd and 4th rows of table 5.7). This is believed to arise from the possibility of an over-estimation of the fill factor  $f$  as determined from the electron micrographs of the specimens concerned. The dark phase in the micrographs may consist of a metal phase and bismuth oxide rich glass

phase<sup>152</sup>. However, an accurate delineation of such micro-structural features is not possible by the experimental technique employed in the present investigation.

Experimentally we observe from the 2nd and 4th rows of table 5.7 that  $\alpha$  values increase with the increase in reduction time in silicate system. However, for glass no.6 it is found that the calculated values show an opposite trend (6th, 8th, 10th and 12th rows of table 5.7). This anomalous behaviour in predicted  $\alpha$  values, though not magnitudinally very different, for the glass no.6 and glass no.2 as mentioned earlier can be explained as follows. Figure 5.33 gives the plots of  $\alpha$  values as calculated by MG theory for different particle sizes in the range of 80 to 160 $\text{\AA}$  with a fixed fill factor of value 0.02. Figure 5.34 shows the plots of  $\alpha$  values as calculated by MG theory for a fixed particle size with different fill factors in the vanadium phosphate as well as in silicate systems. We see from these two figures that fill factor has a more pronounced effect on the calculated  $\alpha$  values than the particle size. The fill factor  $f \propto (\bar{x}/t_{em})$  (equation 5.4) where  $t_{em}$  is the thickness of the specimen under observation in the transmission electron microscope. A value of 1000 $\text{\AA}$  has been assumed for  $t_{em}$  which is the upper limit of electron transmission. However, it is quite likely that it may be less than 1000 $\text{\AA}$ . In that case the calculated  $f$  will be less than the true value and as a result there will be an underestimation of the  $\alpha$  values.

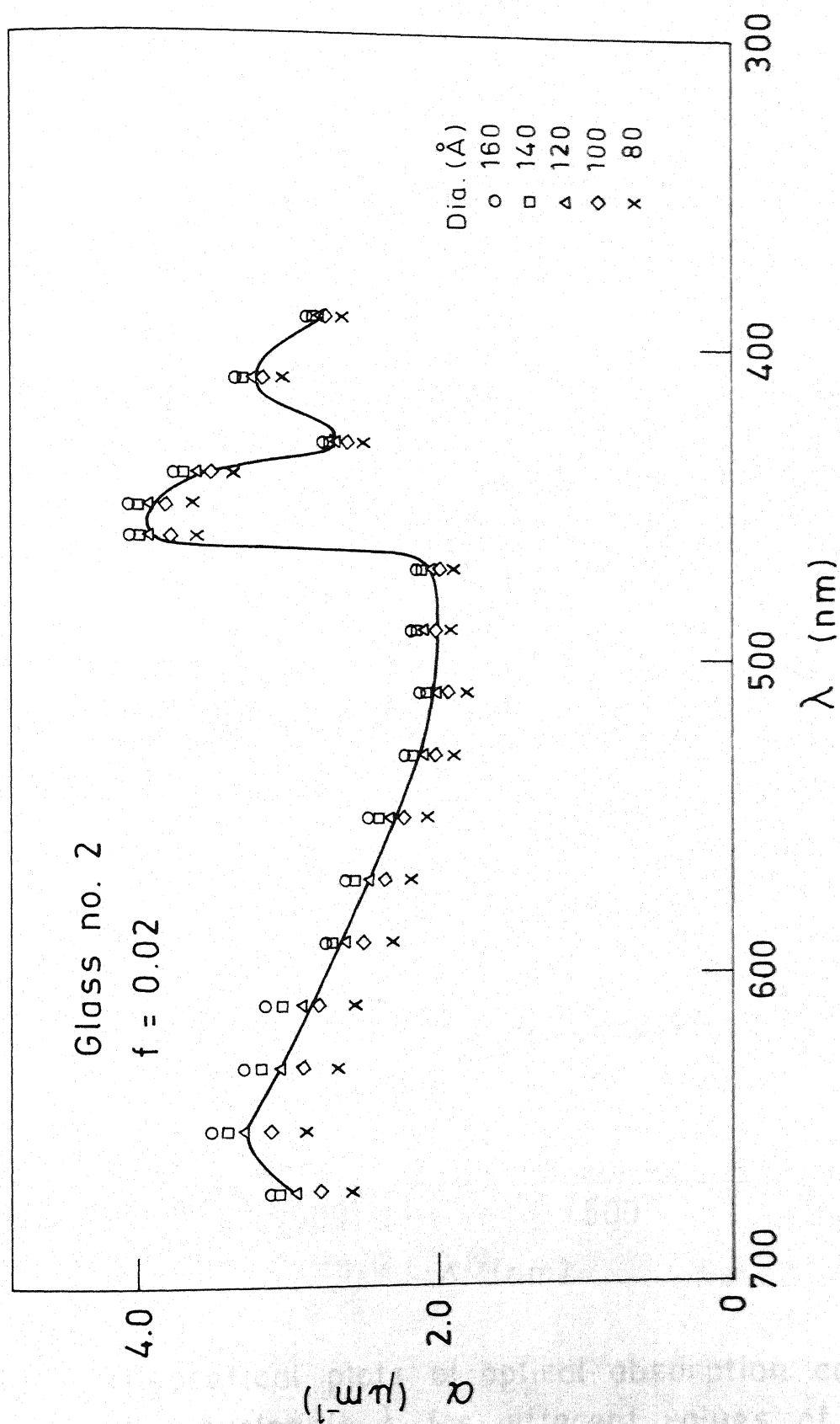


Fig. 5.33 Theoretical plots of optical absorption coefficients  $\alpha$  vs wavelength  $\lambda$  for different particle diameters (calculated by MG Theory).

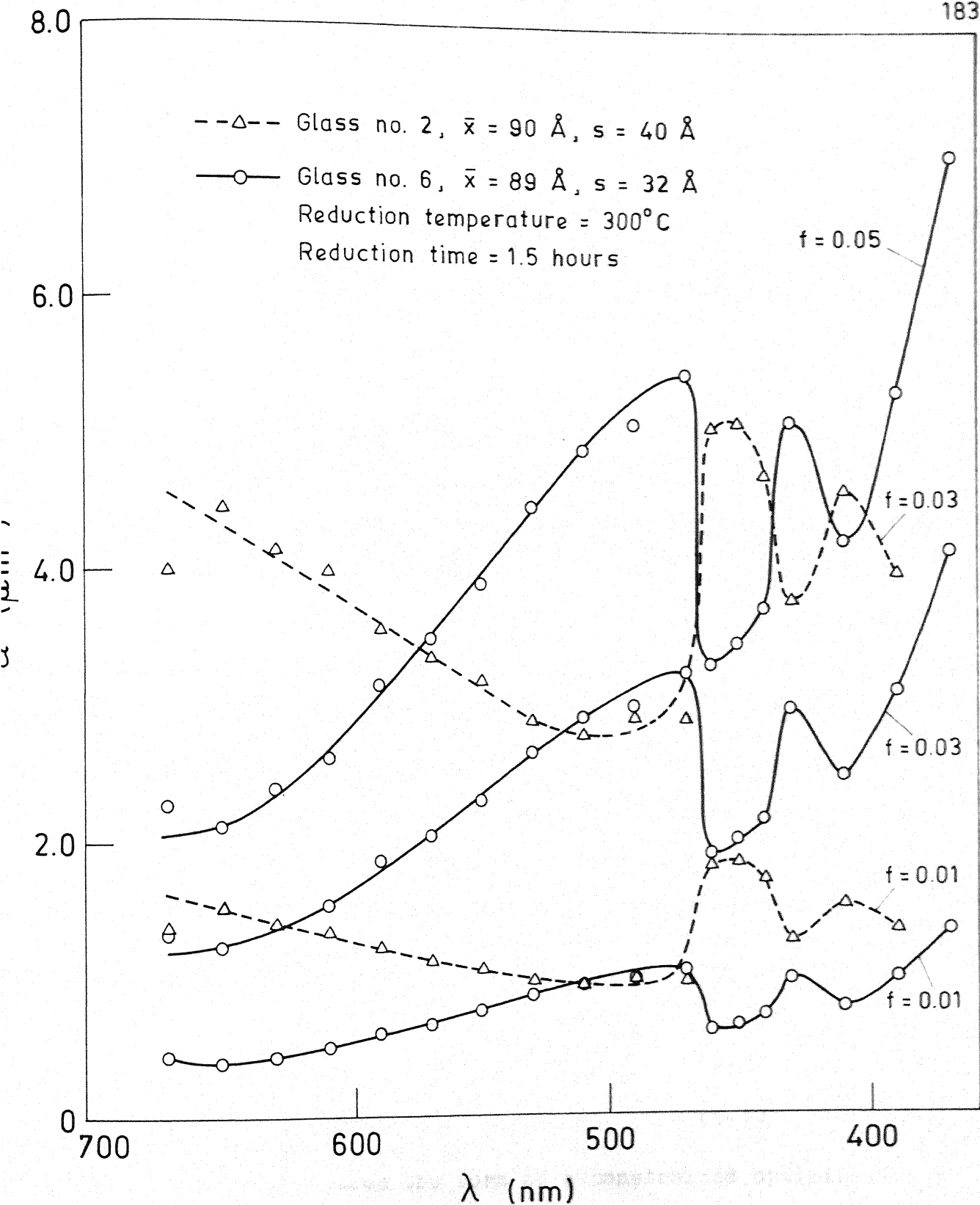


Fig. 5.34 Theoretical plots of optical absorption coefficient  $\alpha$  vs wavelength  $\lambda$  for different values of fill factors. (calculated by MG Theory)

So far we have assumed that the metallic phase consists either of spherical granules of some average particle size or of a distribution of spherical particles (BR and MG-PvS theories). However, the inspection of microstructures (figures 5.5 to 5.16) suggests that elongated interconnected particles are also present. Therefore, the assumption that the metallic bismuth phase consists of  $\xi$  fraction of spheres,  $\zeta$  fraction of single strand chains and  $\chi$  ( $\chi = 1 - \xi - \zeta$ ) fraction of f.c.c. clusters is reasonable. This consideration effectively takes into account the dipole-dipole interactions between the particles as they are closely situated. This is accomplished by replacing the  $L_k$ 's in equation (5.14) by effective depolarisation factors corresponding to the above mentioned geometrical configurations<sup>122</sup>. It has been shown by Granqvist et al.<sup>122</sup> that there exists an optimum combination of  $\xi$ ,  $\zeta$  to obtain the best agreement between experimental and calculated  $\alpha$  values subject to the following constraints,

$$\xi \geq 0 \quad (5.37)$$

$$\zeta \geq 0 \quad (5.38)$$

$$\xi + \zeta \leq 1 \quad (5.39)$$

Thus the problem takes the form of a constrained optimisation. We have chosen the MG-PvS formalism and glass no.2 reduced at 200°C for 2.0 hours for such an analysis.

### 5.5.2 Formulation of constrained optimisation and numerical computation

The objective function to be minimised subjected to the constraints specified in equations (5.37 - 5.39) is given by,

$$f(\vec{X}) = \sum_{\omega=1}^n (\alpha_{\omega}^{\text{MG-PvS}} - \alpha_{\omega}^{\text{exp}})^2 \quad (5.40)$$

where  $\alpha_{\omega}^{\text{MG-PvS}}$  and  $\alpha_{\omega}^{\text{exp}}$  are the theoretical  $\alpha$  values as calculated by MG-PvS theory and the experimentally observed  $\alpha$  values respectively at an angular frequency  $\omega$  and  $n$  being the number of frequencies at which the  $\alpha$  value is calculated.  $\vec{X}$  is a vector consisting of  $\xi, \zeta$  - the optimisation variables. The above constrained optimisation is converted into an equivalent unconstrained optimisation by augmenting the function  $f(\vec{X})$  by a penalty term within the frame work of internal penalty function method<sup>153</sup>. The equivalent function  $\varphi(\vec{X}, r_k)$  is given by,

$$\varphi(\vec{X}, r_k) = f(\vec{X}) - r_k \sum_{j=1}^m \frac{1}{g_j(\vec{X})} \quad (5.41)$$

where  $r_k$  is the penalty parameter,  $g_j(\vec{X}) \leq 0$  is the constraint. In our case the last term of equation (5.41) is given by,

$$\sum_{j=1}^m \frac{1}{g_j(\vec{X})} = \left[ -\frac{1}{\xi} - \frac{1}{\zeta} + \frac{1}{\xi+\zeta-1} \right] \quad (5.42)$$

For evaluating the  $\alpha_w^{MG-PvS}$  by MG-PvS theory  $\bar{\epsilon}_1$  and  $\bar{\epsilon}_2$  will be given by equations (5.30) and (5.31) with  $A_1, B_1, C_1$  and  $D_1$  of equations (5.32) replaced by the following expressions to take into account the  $\xi$  fraction of sphere,  $\tau$  fraction of single strand chain (s.c.) and  $x$  fraction of f.c.c. cluster (f.c.).

$$A_1 = 1 + \frac{2}{3} f[\xi \sum_j w_j \delta'_j|_{\text{sphere}} + \tau \delta'|_{\text{s.c.}} + x \delta'|_{\text{f.c.}}] \quad (5.43a)$$

$$B_1 = \frac{2}{3} f[\xi \sum_j w_j \delta''_j|_{\text{sphere}} + \tau \delta''|_{\text{s.c.}} + x \delta''|_{\text{f.c.}}] \quad (5.43b)$$

$$C_1 = 1 - \frac{1}{3} f[\xi \sum_j w_j \delta'_j|_{\text{sphere}} + \tau \delta'|_{\text{s.c.}} + x \delta'|_{\text{f.c.}}] \quad (5.43c)$$

$$D_1 = \frac{1}{3} f[\xi \sum_j w_j \delta''_j|_{\text{sphere}} + \tau \delta''|_{\text{s.c.}} + x \delta''|_{\text{f.c.}}] \quad (5.43d)$$

where

$\delta'_j|_{\text{sphere}}$ ,  $\delta'|_{\text{s.c.}}$  and  $\delta'|_{\text{f.c.}}$  are respectively the real parts of the polarisability corresponding to spheres, single strand chains and f.c.c. clusters. Similarly,  $\delta''_j|_{\text{sphere}}$ ,  $\delta''|_{\text{s.c.}}$  and  $\delta''|_{\text{f.c.}}$  represent the imaginary parts of the polarisability corresponding to the geometrical configurations - spheres, single strand chains and the f.c.c. clusters.  $\delta'_j$  and  $\delta''_j$  are given by expressions (5.33) to (5.35) by introducing  $L_k$ 's for sphere<sup>122</sup>. The effective depolarisation factors

corresponding to different geometrical configurations have been computed, as we have mentioned in Section 5.4.2, that these are made up of identical spheres<sup>122</sup>. Therefore, in the case of single strand chains and f.c.c. clusters an average particle size has been used to compute the values of  $\delta'$  and  $\delta''$ . After evaluating  $\bar{\varepsilon}_1$  and  $\bar{\varepsilon}_2$  numerically, the  $\alpha$  values are computed from equation (5.36).

#### 5.5.2.1 Numerical scheme

The following iterative scheme is used to optimise the function  $\varphi(\vec{X}, r_k)$ .

- Step 1 : The computation is started with three initial feasible values of  $\vec{X}_1, \vec{X}_2$  and  $\vec{X}_3$  such that the strict inequality constraint is satisfied. An initial value of  $r_1 > 0$  is taken.  $k = 1$  is set.
- Step 2 :  $\varphi(\vec{X}, r_k)$  is minimised using Simplex optimisation technique<sup>153</sup>. Whether the minimised  $\vec{X}_k^*$  obtained corresponds to the minimum of the original problem or not ( $f(\vec{X})$ ) is tested. If so the process is terminated. Otherwise the next step is followed.
- Step 3 : New penalty parameter  $r_{k+1}$  is computed by
- $$r_{k+1} = cr_k, \quad \text{where } c < 1.$$
- Step 4 : With the minimum value of  $\vec{X}_k^*$  and setting  $k = k+1$  step 2 is repeated.



The computer programme in fortran language is given in Appendix 4.

Figure 5.35 shows the plot of  $\alpha$  values as a function of wavelength  $\lambda$  for an optimum combination of 26 percent spheres, 0.6 percent single strand chain and 73.4 percent f.c.c. clusters within an error of  $\pm 4.0$  percent for glass no.2 reduced at  $200^{\circ}\text{C}$  for 2 hours. In this figure are also included the computed values from MG, and MG-PvS theories and the experimental results. Figure 5.35 shows that a better agreement is obtained between theory and experiment when the microstructure is assumed to consist of a combination of spheres, single strand chains and f.c.c. clusters rather than a simple distribution of spheres. It may be mentioned that the above optimisation procedure when applied to the silicate glass system does not bring about any significant improvement in the calculated  $\alpha$  values vis-a-vis the experimental data. This is attributed to the possibility of an overestimation of the fill factor as discussed earlier.

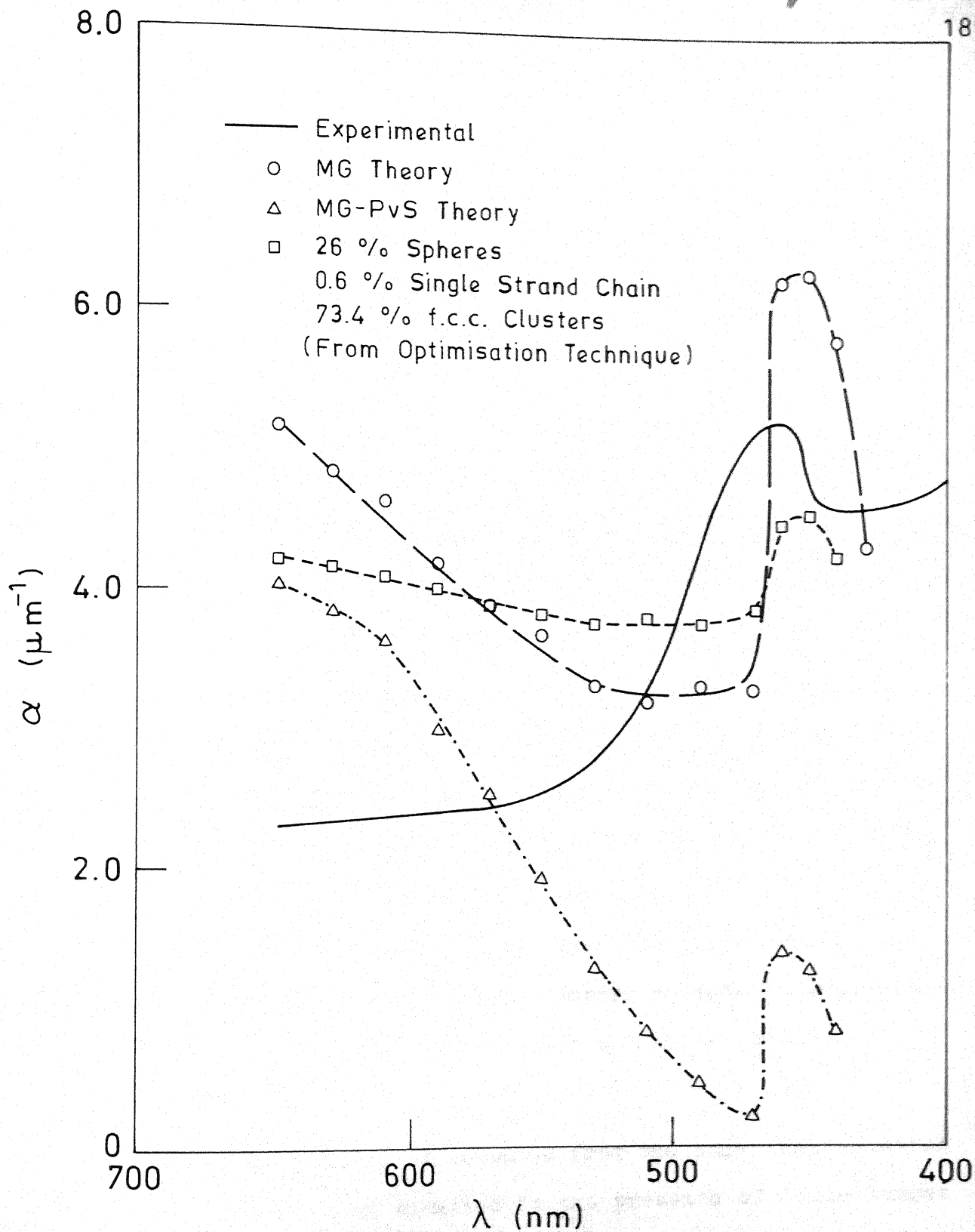


Fig. 5.35

Comparison of experimental absorption coefficient  $\alpha$  with theoretical values computed by different models for glass no. 2 reduced at 200°C for 2.0 hours.

## CHAPTER 6

### CONCLUSIONS

Based on electrical and optical studies of vanadium phosphate as well as silicate glasses containing bismuth the following conclusions are drawn.

- (1) A particle stretching model in which molten metallic granules stretch under the influence of an electric field can explain semi-quantitatively most of the characteristic features of memory switching in oxide glasses containing metallic bismuth granules.
- (2) Depending on the sample thickness the vanadium phosphate glasses containing bismuth can show either memory or threshold switching behaviour.
- (3) The computed current-voltage characteristics especially in the negative resistance region compare reasonably well with the experimental results for vanadium phosphate glasses containing bismuth.
- (4) The switching time as computed from the numerical solution of time dependent heat equation in the presence of Joule losses agrees well with experimental switching time obtained by pulse measurements.

- (5) The switching time as computed from the numerical solution of time dependent stretching of molten metallic bismuth particles in vanadium phosphate system, is found to be very small as compared to the experimentally determined switching time from pulse measurements. However, the fast kinetics of stretching indicates that if the metallic bismuth particles are in a molten state switching time of the order of nanoseconds can be achieved.
- (6) MG, MG-PvS and BR theories predict the optical absorption peak positions which are in fair agreement with the experimentally observed values for both silicate and vanadium phosphate glass systems containing bismuth granules.
- (7) MG theory predicts results with regard to the absorption coefficient  $\alpha$  which are in better agreement with experiment than those obtained from MG-PvS or BR theory in vanadium phosphate glass-metal system.
- (8) A typical computation using constrained optimisation technique indicates that better quantitative agreement (within  $\pm 4$  percent) with experiment over the entire spectral range can be achieved by assuming that the vanadium phosphate glass-metal composites consist of certain fractions of spheres, f.c.c. clusters and single strand chains. The microstructural features of most samples tend to corroborate this model.

## REFERENCES

1. D. Chakravorty, Preparation and Characterization of Materials, ed., C.N.R. Rao and J.M. Honig (Academic Press, London, in press).
2. P.W. McMillan, Glass-Ceramics, 2nd Edition (Academic Press, London, 1979).
3. W.A. Weyl, Coloured glasses, Society of Glass Technology, 1951.
4. G.E. Rindone, J. Am. Ceram. Soc. 45, 7 (1962).
5. S.D. Stookey, U.S. Patent 2515275, 1950.
6. S.D. Stookey, Brit. Patent 635649, 1947.
7. S.D. Stookey, Brit. Patent 752243, 1956.
8. S.D. Stookey and R.D. Maurer, Progress in Ceramic Sciences, Vol. 2 (Pergamon Press, New York, 1962), p. 77.
9. Roger J. Araujo, Treatise on Materials Science and Technology, Vol. 12 (Academic Press, London, 1977), p. 91.
10. W.H. Armistead and S.D. Stookey, U.S. Patent 3923529, 1965.
11. J. Suzuki and M. Kume, U.S. Patent 3617316, 1971.
12. Roger J. Araujo, L.G. Sawchuk and T.P. Seward, U.S. Patent 3703388, 1972.
13. P.W. McMillan, Phys. Chem. Glasses, 17 (5), 193 (1976).
14. Y. Moriya, 10th Int. Congr. Glass, Kyoto (1974).
15. T.P. Seward, Symposium on Photochromic Glasses, Am.Ceram. Soc. Meeting, 76th Chicago, Illinois (1974).
16. S. Sakka, K. Matsusita and K.Kamiya, 10th Int. Congr. Glass, No.5, Kyoto (1974).
17. H. Besen, Proc. XIth Int. Congr. Glass, Vol.3, Prague (1977).
18. George B. Hares and Thomas P. Seward III, J. Non-cryst. Solids, 38 and 39, 205 (1980).

19. George Gliemeroth, J. Non-Cryst. Solids, 38 and 39, 217(1980).
20. R.J. Araujo, R.A. Eppler and E.F. Kruse, U.S. Patent 3,328, 182 (1967).
21. E.L. Swarts and J.P. Pressau, J. Am. Ceram. Soc. 48, 333 (1965).
22. G.S. Meiling, U.S. Patent 3615, 771 (1971).
23. R.J. Araujo, G.H. Beall and L.G. Sawchuk, U.S. Patent 3923529 (1975).
24. L.G. Sawchuk and S.D. Stookey, U.S. Patent 3293052 (1966).
25. S. Sakka and J.D. MacKenzie, J. Am. Ceram. Soc. 35, 553 (1972).
26. Thomas P. Seward III, J. Appl. Phys. 46(2), 689 (1975).
27. L.J. Randall and T.P. Seward III, U.S. Patent 3208860 (1965).
28. J.J. Hammel and T. McGary, Reactivity of Solids, ed. J.W. Mitchell (Wiley, New York, (1969) p. 695.
29. T.P. Seward III, J. Non-cryst. Solids 40, 499 (1980).
30. S.D. Stookey, G.H. Beall and J.E. Pearson, J. Appl. Phys. 49, 5114 (1978).
31. N.F. Borrelli, J.B. Chodak, D.A. Nolan and T.P. Seward III, J. Opt. Soc. Am. 69, 1514 (1979).
32. John C.C. Fan and Paul M. Zavracky, Appl. Phys. Lett. 29(8), 478 (1976).
33. John C.C. Fan and Steven A. Spura, Appl. Phys. Lett. 30(10), 511 (1977).
34. H.G. Craighead and R.A. Buhrman, Appl. Phys. Lett. 31(7), 423 (1977).
35. G.A. Niklasson and C.G. Granqvist, J. Appl. Phys. 50(8), 5500 (1979).
36. H. Schulz, Glashütte, 66, 685 (1936).
37. L.J. Dykstra and E.M. Meyer, U.S. Patent 2274955 (1942).
38. T.W.H. Ward, U.S. Patent 2280135 (1942).

39. R.L. Green and B. Blodgett, J. Am. Ceram. Soc. 31, 89 (1948).
40. K.B. Blodgett, J. Am. Ceram. Soc. 34, 14 (1951).
41. D. Chakravorty, French Patent 31218 (1972).
42. D. Chakravorty, J. Non-cryst. Solids 15, 191 (1974).
43. G.C. Das, T.K. Reddy and D. Chakravorty, J. Mat. Sc. 13, 3211 (1978).
44. D. Chakravorty, A.R. Haranahalli and D. Kumar, Phys. Stat. Solidi (a), 51, 275 (1979).
45. D. Chakravorty, A.K. Bandopadhyay and V.K. Nagesh, J. Phys. D: Appl. Phys. 10, 2077 (1977).
46. D. Chakravorty and S. Chakrabarti, J. Non-cryst. Solids. 38 and 39, 295 (1980).
47. B. Abeles, Sheng Ping, M.D. Coutts and Y. Arie, Adv. Phys. 24, 407 (1975).
48. D. Chakravorty, B.N. Keshavram and A. Venkateswaran, J. Mat. Sc. 14, 2991 (1979).
49. D. Chakravorty and R. Bhatnagar, Proc. Int. Symp. Fibres and Composites, New Delhi, 1, 71 (1976).
50. D. Chakravorty, Appl. Phys. Lett. 24(2), 62 (1974).
51. D. Chakravorty and C.S. Murthy, J. Phys. D: Appl. Phys. 8, L162 (1975).
52. P. Hing and P.W. McMillan, J. Mat. Sc. 8, 1041 (1973).
53. B.N. Keshavram, M.Tech. Thesis, IIT Kanpur (1978).
54. A. Venkateswaran, M.Tech. Thesis, IIT Kanpur (1979).
55. S.R. Ovshinsky, Electronics, 32, 76 (1959).
56. A.D. Pearson, W.R. Northover, Jacob F. Dewald and W.F. Peck, Jr., Adv. Glass Technology (Plenum Press, New York, 1962), p. 357.
57. S.R. Ovshinsky, Phys. Rev. Lett. 21, 1450 (1968).
58. D. Adler, H.K. Henisch and N.F. Mott, Rev. Mod. Phys. 50, 209 (1978).

59. M. Kastner, D. Adler and H. Fritzsche, Phys. Rev. Lett. 37, 1504 (1976).
60. R.A. Street, Adv. Phys. 25, 397 (1976).
61. R. Grigorovici, Thin Solid Films, 9, 1(1971).
62. B.T. Kolomiets, Amorphous and Liquid Semiconductors, ed. J. Stuke and W. Brenig (Taylor and Francis, London, 1974), p. 189.
63. B.T. Kolomiets, T.N. Mamontova and A.A. Babaev, Amorphous and Liquid Semiconductors, ed. M.H. Cohen and G. Lucovsky (North Holland, Amsterdam, 1972), p. 1004.
64. J.M. Marshal, C. Main and A.E. Owen, Amorphous and Liquid Semiconductors, ed. M.H. Cohen and G. Lucovsky (North Holland, Amsterdam, 1972), p. 760.
65. C. Main and A.E. Owen, Amorphous and Liquid, Semiconductors ed. J. Stuke and W. Brening (Taylor and Francis, London, 1974) p. 783.
66. S.G. Bishop, U. Strom and P.C. Taylor, Phys. Rev. Lett. 39, 1346 (1975).
67. A.E. Owne, J.M. Robertson and C. Main, J. Non-cryst. Solids 32, 29(1979).
68. H. Fritzsche, Amorphous and Liquid Semiconductors ed. J. Tauc (Plenum Press, New York, 1974).
69. W.D. Buckley and S.H. Holmberg, Solid Stat. Electronics 18, 127 (1975).
70. A.R. Hilton, C.E. Jones and M. Brau, Phys. Chem. Glasses 7, 105 (1966).
71. J.A. Savage, J. Non-cryst. Solids 11, 121 (1972).
72. H.J. Stocker, C.A. Barlow and D.F. Weirauch, J. Non-cryst. Solids 4, 523 (1970).
73. H. Lueder and E. Epenke, Z. Tech. Phys. 16, 11(1935).
74. B.K. Ridley, Proc. Phys. Soc. 82, 954 (1963).
75. A.C. Warren, J. Non-cryst. Solids 4, 613 (1970).



76. D.C. Thomas and J.C. Male, Amorphous and Liquid Semiconductors ed. M.H. Cohen and G. Lucovsky (North Holland, Amsterdam, 1972) p. 522.
77. C. Popescu and H. Croitrou, Amorphous and Liquid Semiconductors ed. M.H. Cohen and G. Lucovsky (North Holland, Amsterdam, 1972), p. 531.
78. J.M. Robertson and A.E. Owen, J. Non-cryst. Solids 8-10, 939 (1972).
79. J. Allison, V.R. Dawe and P.N. Robson, J. Non-cryst. Solids 8-10, 563 (1972).
80. D.M. Kroll and M.H. Cohen, Amorphous and liquid semiconductors ed. M.H. Cohen and G. Lucovsky (North Holland, Amsterdam, 1972) p. 544.
81. A.J. Hughes, P.A. Holland and A.H. Lellington, J. Non-cryst. Solids 17, 89 (1975).
82. P. Esqueda and H.K. Henisch, J. Non-cryst. Solids 22, 97 (1976).
83. J.K. Higgins, B.K. Temple and J.E. Lewis, J. Non-cryst. Solids 23, 187 (1977).
84. N.F. Mott, Contemp. Phys. 10, 125 (1969).
85. H.K. Henisch, Sci. Am. 221, 30 (1969).
86. N.F. Mott and E.A. Davis, Electronic Processes in Non-crystalline Materials, 2nd Edition (Clarendon Press, Oxford, 1979), p. 509.
87. K.E. Peterson and D. Adler, J. Appl. Phys. Lett. 25, 211 (1974).
88. K.E. Peterson and D. Adler, J. Appl. Phys. 47, 256 (1976).
89. R.W. Pryor and H.K. Henisch, J. Non-cryst. Solids 7, 184 (1972).
90. G.F. Vendura and H.K. Henisch, J. Non-cryst. Solids 11, 105 (1972).
91. G.C. Vezzoli, L.W. Doremus and P.J. Walsh, Amorphous and Liquid Semiconductors, ed. J. Stuke and W. Brenig (Taylor and Francis, London, 1974) p. 651.

92. P.J. Walsh and G.C. Vezzoli, *Amorphous and Liquid Semiconductors* ed. J. Stuke and H. Brening (Taylor and Francis, London, 1974), p.1391.
93. S.R. Ovshinsky and P.H. Klose, *J. Non-cryst. Solids* 8-10, 892 (1972).
94. H. Fritzsche and S.R. Ovshinsky, *J. Non-cryst. Solids* 2, 148 (1970).
95. E. Ahilea and A.A. Hirsch, *J. Appl. Phys.* 42, 5601 (1971).
96. A.W. Adamson, *Physical Chemistry of Surfaces* (Interscience, New York, 1967).
97. T. Kaplan and D. Adler, *Appl Phys. Lett* 19, 418(1971).
98. E. Kreyszig, *Adv. Engg. Math* (Wiley Eastern Ltd., New Delhi, India, 1971).
99. J.M. McCormick and M.G. Salvadori, *Numerical Methods in Fortran* (Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1964).
100. W.D. Kingery, *Introduction to Ceramics* (Wiley, New York, 1967).
101. S.J. Peppiatt, *Proc. Roy. Soc.* 345A, 1642 (1975).
102. C.D. Hodgman, *Handbook of Chemistry and Physics* (Chemical Rubber Pub. Co., Cleveland, Ohio, 1962).
103. D. Turnbull, *J. Chem. Phys.* 18, 768 (1950).
104. J.Crank and P. Nicolson, *Proc. Phil. Soc.* 43, 50(1947).
105. L. Fox, *Numerical Solution of Ordinary and Partial Differential Equations*, ed. L. Fox (Pergamon Press, London, 1962) p. 235.
106. M.W. Davies, B. Kerrison, W.E. Cross, M.J. Robson and D.F. Wichall, *J. Iron and Steel Inst.* 208, 348 (1970).
107. D. Kumar, Ph.D. Thesis, IIT Kanpur (1980).
108. *Selected Powder Diffraction Data for Minerals*, (Published by Joint Committee on Powder Diffraction Standards, Pennsylvania, U.S.A., 1979).

109. R.R. Sutherland, J. Phys. D: Appl. Phys. 4, 468 (1974).
110. G. Dearnaley, D.V. Morgan and A.M. Stonehan, J. Non-cryst. Solids 4, 593 (1970).
111. S.W. Yuan, Foundation of Fluid Mechanics (Prentice Hall, India, Pvt.Ltd., New Delhi, 1976).
112. W.F. Ames, Numerical Methods for Partial Differential Equations (Thomas Nelson and Sons Ltd., London, 1969).
113. R.W. Doremus, J. Chem. Phys. 40, 2389 (1964).
114. R.W. Doremus, J. Chem. Phys. 42, 414 (1965).
115. H. Rawson, Phys. Chem. Glasses 6, 81 (1965).
116. D. Chakravorty, A. Shuttleworth and P.H. Gaskell, J. Mat. Sc. 10, 799 (1975).
117. P. Sarkar, M.Tech. Thesis, IIT Kanpur (1981).
118. W. Hampe, Z. Phys 152, 470 (1958).
119. R.W. Cohen, G.D. Cody, M.D. Coutts and B. Abeles, Phys. Rev.B 8, 3689 (1973).
120. P.H. Lissberger and R.G. Nelson, Thin Solid Films, 21, 159 (1974).
121. P.H. Lissberger and P.W. Saunders, Thin Solid Films, 34, 323 (1976).
122. C.G. Granqvist and O. Hunderi, Phys. Rev. B 16(8), 3513 (1977).
123. C.G. Granqvist and O. Hunderi, J. Appl. Phys. 51(3), 1751(1980).
124. C.G. Granqvist and G.A. Niklasson, J. Appl. Phys. 49(6), 3512(1978).
125. C.G. Granqvist, N. Calander and O. Hunderi, Solid Stat. Commun. 31, 249 (1979).
126. S. Norman, T. Andersson and C.G. Granqvist, Phys. Rev. B 18(2), 674 (1978).

127. B. Abeles and J.I. Gittleman, Appl. Opt. 15, 2328 (1976).
128. C.G. Granqvist and O. Hunderi, Phys. Rev. B 18(6), 2897 (1978).
129. C.G. Granqvist, J. Appl. Phys. 50(4), 2916 (1979).
130. J.I. Gittleman, B. Abeles, P. Zanzucchi and Y. Arie, Thin Solid Films 45, 9(1977).
131. D.R. McKenzie and R.C. McPhedran, AIP, Conf. Proc. 40, 283 (1978).
132. C.G. Granqvist and O. Hunderi, Z. Physik B 30, 47(1978).
133. C.G. Granqvist and O. Hunderi, J. Appl. Phys. 50(2), 1058 (1979).
134. L. Genzel, T.P. Martin and U. Kreibig, Z. Physik B 21, 339 (1974).
135. M.A. Smithard, Solid Stat. Commun. 13, 153 (1973).
136. R.T. DeHoff and F.N. Rhines, Quantative Microscopy (McGraw-Hill, New York, 1968).
137. G. Mie, Ann. Phys. 25, 377 (1908).
138. C.R. Bamford, Colour Generation and Control in Glasses, Glass Science and Technology 2 (Elsevier Sci. Pub. Co., Amsterdam, 1977).
139. R. Gans, Ann. Phys. 29, 277 (1909).
140. R. Gans, Ann. Phys. 37, 883 (1912).
141. J.C. Maxwell-Garnett, Phil. Trans. Roy. Soc. London 203, 385 (1904).
142. L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936).
143. D. Polder and J.H. van Santen, Physica (Utrecht) 12, 257 (1946).
144. D.A.G. Bruggeman, Ann. Phys. (Leipz.) 24, 636 (1935).
145. O. Hunderi, Phys. Rev. B 7, 3419 (1973).
146. G.A. Niklasson, C.G. Granqvist and O. Hunderi, Appl. Opt. 20(1), 26 (1981).

147. H.C. Van de Hulst, Light Scattering by Small Particles (Wiley, New York, 1957).
148. American Institute of Physics Handbook, 3rd Edition, ed. Dwight E. Gray (McGraw-Hill Book Co. New York, 1972), p. 6-128.
149. J. Toots and L. Marton, J. Opt. Soc. Am. 59(10), 1305 (1969).
150. C. Kittle, Introduction to Solid State Physics (Wiley Eastern Pvt.Ltd., New Delhi, 1974).
151. A. Mansingh, R.P. Tandon and J.K. Vaid, J. Phys. C: Solid State Phys. 8, 1023 (1975).
152. D. Chakravorty, C.S. Vithlani and G.K. Mehta, J. Mat.Sc. 13, 1438 (1978).
153. S.S. Rao, Optimization, Theory and Practice (Wiley Eastern Ltd., New Delhi, 1979).

## APPENDIX 1

PROGRAMME FOR COMPUTING THE TEMPERATURE PROFILE  
TO REACH THE MELTING POINT OF BISMUTH AT THE  
CENTRE OF THE SAMPLE BY SOLVING HEAT EQUATION  
BY RUNGE-KUTTA-NYSTROM METHOD

\*\*\*\*\*  
DA- AVERAGE PARTICLE DIA. IN METER  
CK(I)- SEPERATION TO DIA. RATIO  
TMB-MELTING TEMP OF BISMUTH

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-----
DIMENSION E(25),DA(50)
COMMON/A1/E,THIC,K
COMMON/A3/TPI,TMB,TI,TMX,ND
COMMON/A5/DIFT,DIFT1,THICP,THICN,DIFTP,DIFTN
READ12,NA,NC,ND
12  FORMAT(3I3)
   PRINT5,NA,NC,ND
5   FORMAT(50X,3I3/1X,130(1H-))
   DA(1)=700.E-10
   DO 10I=2,NA
10  DA(I)=DA(I-1)+100.E-10
   READ16,(E(K),K=1,NC)
16  FORMAT(5E7.1)
   TI=433.
   PRINT 46,TI
46  FORMAT(44X,'AMBIENT TEMP IN DEG KELVIN=',E15.8/44X,20(1H-))
   DO 40 I=1,NA
   PRINT45,DA(I)
45  FORMAT(45X,'AVERAGE PARTICLE DIA IN METER=',E15.8)

```

-----  
COMPUTATION OF SIZE DEPENDENT MELTING POINT OF BISMUTH  
-----

```

ABI=208.87
VA=ABI/9.67
VB=ABI/10.
TM=271.0+273.
AD1=DA(I)*1.E2/2.
DC=(VA-(VB**2)/(VB-VA))/AD1
DB=-(2.*54.4)/(10.2*ABI*4.184E07)
TMB=TM*EXP(DB*DC)
PRINT 700,TMB
700 FORMAT(40X,'MELTING TEMP. OF BISMUTH DEPENDING ON RADIUS=',F6.2)
   DO 70 K=1,NC
   PRINT75,E(K)
75  FORMAT(40X,'FIELD IN VOLT PER METER=',E15.8)
   THIC=5.E-6
   TMX=TMB+5.
   TPI=1.E2
   CALL DCT
   IF(DIFT1.LE.0.1)GO TO 70
   IF(DIFT.LT.0.)GO TO 61
62  THIC=THIC+1.E-6
   CALL DCT
   IF(DIFT1.LE.0.1)GO TO 70
   IF(DIFT.LT.0.)GO TO 63
   GO TO 62
61  THIC=THIC*.9
   CALL DCT
   IF(DIFT1.LE.0.1)GO TO 70
   IF(DIFT.GT.0.)GO TO 63
   GO TO 61

```

-----  
INTERPOLATION OF THICKNESS BY REGULA FALSI METHOD  
-----

```

63  THIC=(THICP*DIFTN-THICN*DIFTP)/(DIFTN-DIFTP)
   CALL DCT
   IF(DIFT1.LE.0.1)GO TO 70

```

```

GO TO 63
CONTINUE
PRINT110
FOR4AT(IX,130(1H*))
PRINT130
FOR4AT(IX,130(1HB))
CONTINUE
STOP
END

```

\*\*\*\*\*

SOLUTION OF SECOND ORDER DIFF. HEAT EQ. BY 4TH ORDER RUNGE KUTTA  
 NYSFROM METHOD  
 TP(1)-FIRST DERIVATIVE OF TEMPERATURE  
 T(L)-TEMPERATURE IN DEGREE KELVIN  
 SUBROUTINE DCT

```

-----
DIMENSION E(25)
COMMON/A1/E,THIC,K
COMMON/A3/TPI,TMB,TI,TMX,ND
COMMON/A4/DIF,DIF1,TPP,TPN,DIFP,DIFN
COMMON/A5/DIFT,DIFT1,THICP,THICN,DIFTP,DIFTN
CALL GOPES
IF(DIF1.LE.0.1)GO TO 74
IF(DIF.LT.0.)GO TO 12
TPI=TPI*.9
CALL GOPES
IF(DIF1.LE.0.1)GO TO 74
IF(DIF.LT.0.)GO TO 16
GO TO 15
TPI=TPI*1.1
CALL GOPES
IF(DIF1.LE.0.1)GO TO 74
IF(DIF.GT.0.)GO TO 16
GO TO 12

```

-----  
 INTERPOLATION OF FIRST ORDER DERIVATIVE OF TEMPERATURE  
 BY REGULA FALSI METHOD  
 -----

```

TPI=(TPP*DIFN-TPN*DIFP)/(DIFN-DIFP)
CALL GOPES
IF(DIF1.LE.0.1)GO TO 74
GO TO 16
IF(DIFT.GT.0.) TPI=TPI*.9
RETURN
END

```

\*\*\*\*\*

SUBROUTINE GOPES

```

-----
DIMENSION E(25),TP(200),T(200)
COMMON/A1/E,THIC,K
COMMON/A2/TT,FUN
COMMON/A3/TPI,TMB,TI,TMX,ND
COMMON/A4/DIF,DIF1,TPP,TPN,DIFP,DIFN
COMMON/A5/DIFT,DIFT1,THICP,THICN,DIFTP,DIFTN
BND=ND
H=1./BND
NN=ND+1
TP(1)=TPI
T(1)=TI
DO 60 L=2,NN
TT=T(L-1)
IF(TT.LT.50.)TPI=TPI+1.E2

```



```

70      GO TO 63
      CONTINUE
      PRINT110
110     FORMAT(IX,130(1H*))
      PRINT130
130     FORMAT(IX,130(1HB))
40      CONTINUE
      STOP
      END

```

\*\*\*\*\*

SOLUTION OF SECOND ORDER DIFF. HEAT EQ. BY 4TH ORDER RUNGE  
 NYSTRON METHOD  
 TP(1)-FIRST DERIVATIVE OF TEMPERATURE  
 T(1)-TEMPERATURE IN DEGREE KELVIN  
 SUBROUTINE DCT

```

-----
      DIMENSION E(25)
      COMMON/A1/E,THIC,K
      COMMON/A3/TP1,TMB,TI,TMX,ND
      COMMON/A4/DIF,DIF1,TPP,TPN,DIFP,DIFN
      COMMON/A5/DIFT,DIFT1,THICP,THICN,DIFTP,DIFTN
      CALL GOPES
      IF(DIF1.LE.0.1)GO TO 74
      IF(DIF.LT.0.)GO TO 12
15      TP1=TP1*.9
      CALL GOPES
      IF(DIF1.LE.0.1)GO TO 74
      IF(DIF.LT.0.)GO TO 16
      GO TO 15
12      TP1=TP1*1.1
      CALL GOPES
      IF(DIF1.LE.0.1)GO TO 74
      IF(DIF.GT.0.)GO TO 16
      GO TO 12

```

-----  
 INTERPOLATION OF FIRST ORDER DERIVATIVE OF TEMPERATURE  
 BY REGULA FALSI METHOD  
 -----

```

16      TPI=(TPP*DIFN-TPN*DIFP)/(DIFN-DIFP)
      CALL GOPES
      IF(DIF1.LE.0.1)GO TO 74
      GO TO 16
74      IF(DIFT.GT.0.) TPI=TP1*.9
      RETURN
      END

```

\*\*\*\*\*

SUBROUTINE GOPES

```

-----
      DIMENSION E(25),TP(200),T(200)
      COMMON/A1/E,THIC,K
      COMMON/A2/TT,FUN
      COMMON/A3/TP1,TMB,TI,TMX,ND
      COMMON/A4/DIF,DIF1,TPP,TPN,DIFP,DIFN
      COMMON/A5/DIFT,DIFT1,THICP,THICN,DIFTP,DIFTN
      BND=ND
      H=1./BND
      NN=ND+1
30      TP(1)=TP1
      T(1)=TI
      DO 60 L=2,NN
      TT=T(L-1)
      IF(TT.LT.50.)TPI=TP1+1.E2

```

```

IF(TT.LT.50.)GO TO 30
CALL ROSE
AA=(H/2.)*FUN
BITA=(H/2.)*(TP(L-1)+AA/2.)
TI=T(L-1)+BITA
IF(TT.LT.50.)TPI=TPI+1.E2
IF(TT.LT.50.)GO TO 30
CALL ROSE
BB1=(H/2.)*FUN
DEL=H*(TP(L-1)+BB1)
TI=T(L-1)+DEL
IF(TT.LT.50.)TPI=TPI+1.E2
IF(TT.LT.50.)GO TO 30
CALL ROSE
DD=(H/2.)*FUN
AK=1./3.*(AA+2.*BB1)
AKS=1./3.*(AA+4.*BB1+DD)
T(L)=T(L-1)+H*(TP(L-1)+AK)
TP(L)=TP(L-1)+AKS
60  CONTINUE
    DIF=T(NN)-T(1)
    DIF1=ABS(DIF)
    IF(DIF.GT.0.)GO TO 20
    TPN=TP(1)
    DIFN=DIF
    GO TO 25
20  TTP=TP(1)
    DIFP=DIF
25  IF(DIF1.GT.0.1)GO TO 73
    NN1=(NN+1)/2
    DIFT=IMB-T(NN1)
    DIFT1=ABS(DIFT)
    IF(DIFT.GT.0.)GO TO 40
    THICN=THIC
    DIFTN=DIFT
    GO TO 45
40  THICP=THIC
    DIFTP=DIFT
45  IF(DIFT1.GT.0.1)GO TO 73
    PRINT135,THIC
135  FORMAT(48X,'THICKNESS IN METER=',E15.8/48X,18(1H-))
    PRINT700,(T(L),L=1,NN)
700  FORMAT(1X,8E15.8)
    PRINT105
105  FORMAT(2X,128(1H-))
73  RETURN
    END

```

\*\*\*\*\*

SUBROUTINE ROSE

```

-----
DIMENSION E(25)
COMMON/A1/E,THIC,K
COMMON/A2/TT,FUN
SIG=-(2.3*1.25*1000./TT)
SIG1=(100./1.334)*EXP(SIG)
FUN=-(THIC**2/1.6744)*SIG1*E(K)**2
RETURN
END

```

## APPENDIX 2

PROGRAMME FOR COMPUTING THE I-V CHARACTERISTICS OF  
 VANADIUM PHOSPHATE GLASS CONTAINING BISMUTH AND DETERMINATION  
 OF TEMPERATURE PROFILE BY SOLVING TIME DEPENDENT HEAT EQUATION  
 \*\*\*\*\*  
 DA(1) AVERAGE PARTICLE DIAMETER IN METER  
 CK(J) SEPERATION TO DIA RATIO  
 TMB-MELTING TEMP OF BISMUTH

```

-----
DIMENSION TI1(100),TI2(100)
DIMENSION DA(50),CK(50),VAP(100),CUR(100)
COMMON/A1/THIC,BD,DM,ICOND,ROHM
COMMON/A2/DIF,DIF1,TKN,TKP,TIME,TK,TI1,E,H,TI2,M,TMB
COMMON/A3/TT,SIGT
DATA NA,NB,ND/1,6,10/
PRINT5,NA
5  FORMAT(50X,13/1X,130(1H-))
   DA(1)=800.E-10
   DO 10 I=2,NA
10  DA(I)=DA(I-1)+100.E-10
   CK(1)=0.02
   DO 20 J=2,NB
20  CK(J)=CK(J-1)+0.01
   CONTINUE
   TI=309.
   TK=0.1
   THIC=45.E-6
   RS=100.
   RSD=30.
   AREA=16.E-6
   PRINT 900,AREA
900  FORMAT(50X,'AREA=',E12.4)
   ROHM=(RSD*AREA)/THIC
   TIMX=(THIC**2*(2.87E03*0.16*4.184E03))/TK
   PRINT 2,THIC,TIMX
2    FORMAT(20X,'THICKNESS IN METER=',E12.4,5X,'MAX. TIME   =',E12.4)
   H=0.1
   PRINT 46,TI
46   FORMAT(44X,'AMBIENT TEMP IN DEG KELVIN=',E15.8/44X,20(1H-))
   ICOND=1
   TT=TI
   CALL ROSE
   REST=(1./SIGT)*(THIC/AREA)
   PRINT 47,REST
47   FORMAT(40X,'RESISTANCE AT ROOM TEMP.=',F8.2)
   DO 40 I=1,NA
   PRINT45,DA(1)
45   FORMAT(45X,'AVERAGE PARTICLE DIA IN METER=',E15.8)
-----
COMPUTATION OF SIZE DEPENDENT MELTING POINT OF BISMUTH
-----
ABI=208.98
VA=ABI/9.67
VB=ABI/10.
TM=271.+273.
AD1=DA(1)*1.E2/2.
DC=(VA-(VB**2)/(VB-VA))/AD1
DB=-(2.*54.4)/(10.2*ABI*4.184E07)
TMB=TM*EXP(DB*DC)
PRINT 700,TMB
700  FORMAT(40X,'MELTING TEMP. OF BISMUTH DEPENDING ON RADIUS=',F6.2)
   DO50 J=1,NB
   PRINT55,CK(J)
55   FORMAT(50X,'RATIO OF PARTICLE SEPERATION TO DIA=',F9.3)
   M=6
   TIME=7.E-5
   TI2(1)=TI
   DO 11 K1=2,11
   TI2(K1)=TI2(K1-1)

```

```

11  CONTINUE
    BD=THIC
    DM=0.
    MD1=MD+1
    M4=0
C
C-----
C  COMPUTATION OF CRITICAL FIELD V/METRE
C-----
    P=1.+CK(J)
    C=4.*0.0544/(0.885418E-11*30.*(DA(I)/2.))
    E=SQRT(C*(P-SQRT(P)))
    VAPP=(THIC*E)/(1.+1./CK(J))
    VAP(1)=VAPP/10.
    DO 86 L=2,10
    VAP(L)=VAP(L-1)+VAPP/10.
86  CONTINUE
    DO 85 L=1,10
    CUR(L)=VAP(L)/REST
85  CONTINUE
    PRINT*,(VAP(L),CUR(L),L=1,10)
    GO TO 72
42  M4=M4+1
    IF(M4.EQ.1)GO TO 780
    GO TO 770
780  SUM=0.
    M2=M
    DO 781 K8=1,M2
    K9=0
    T4=TI2(K8)
782  K9=K9+1
    T5=T4+(TI2(K8+1)-TI2(K8))*0.1
    TT=(T4+T5)/2.
    ICOND=1
    CALL ROSE
    T4=T5
    SUM=SUM+(1./SIGI)*0.01*THIC
    IF(K9.LE.9)GO TO 782
781  CONTINUE
    RD=SUM*2./AREA
    SI=VAPP/(RD+RS)
    SV=VAPP
    PRINT*,RD,TIME
    PRINT 783,SI,SV
783  FORMAT(15X,'OFF STATE CURRENT AMP.=',E15.8,15X,'POT. DROP
    1ACROSS SAMPLE VOLT=',E15.8)
    PRINT110
    GO TO 72
770  M2=M
    XL=M
    BD=XL*0.1*THIC*2.
    DM=THIC-BD
    RM=(ROHM*DM)/AREA
    SUM=0.
    DO 90 K8=1,M2
    K9=0
    T4=TI2(K8)
91  K9=K9+1
    T5=T4+(TI2(K8+1)-TI2(K8))*0.1
    TT=(T4+T5)/2.
    ICOND=1
    CALL ROSE
    T4=T5
    SUM=SUM+(1./SIGI)*0.01*THIC
    IF(K9.LE.9)GO TO 91
90  CONTINUE
    RD=SUM*2./AREA
    ED=(VAPP*(1.+1./CK(J))*RD)/(BD*(RM+RS+RD))
    EM=(VAPP*ROHM)/(AREA*(RM+RS+RD))

```

```

E=(BD*ED+DM*EM)/THIC
PRINT 972, BD, RD, ED, DM, RM, EM, TIME
972  FORMAT(10X, 7E16.7)
SI=VAPP/(RD+RM+RS)
SV=SI*(RD+RM)
PRINT 94, SI, SV
94  FORMAT(20X, 'CURRENT AMP.=', E15.8, 20X, 'POT. DROP ACROSS
1SAMPLE VOLTS=', E15.8)
PRINT 110
72  PRINT 75, E
75  FORMAT(40X, 'FIELD IN VOLT PER METER=', E15.8)
IF(M.EQ.1)GO TO 80
DO 12 K1=1, 11
12  T11(K1)=TI2(K1)
CONTINUE
IF(TIME.GT.TIMX)GO TO 50
CALL TEMEV
IF(DIF1.LE.1.0)GO TO 41
506  IF(DIF.LE.0.)GO TO 500
TIME=TIME+0.1*TIME
IF(TIME.GT.TIMX)GO TO 50
CALL TEMEV
IF(DIF1.LE.1.0)GO TO 41
IF(DIF.LT.0.)GO TO 505
500  GO TO 506
TIME=TIME+0.1*TIME
IF(TIME.GT.TIMX)GO TO 50
CALL TEMEV
IF(DIF1.LE.1.0)GO TO 41
IF(DIF.GT.0.)GO TO 505
GO TO 500
-----
METHOD OF BISECTION
-----
505  TIME=(TKN+TKP)/2.
IF(TIME.GT.TIMX)GO TO 50
CALL TEMEV
IF(DIF1.LE.1.0)GO TO 41
41  GO TO 505
M=M-1
IF(M.GE.2)GO TO 42
IF(M.EQ.1)GO TO 770
80  RM=(ROHM*THIC)/AREA
SI=VAPP/(RM+RS)
SV=SI*RM
PRINT*, RM, TIME
PRINT 761, SI, SV
761  FORMAT(15X, 'ON STATE CURRENT AMP.=', E15.8, 15X, 'POT. DROP
50  1ACROSS SAMPLE VOLT=', E15.8)
CONTINUE
PRINT 110
100  FORMAT(IX, 130(1H(*)))
40  CONTINUE
STOP
END
*****
C  SUBROUTINE TEMEV
C  GAUSS ITERATION
C  -----
DIMENSION T11(100), T1(100), T2(100), BN(100), TI2(100)
COMMON/A1/THIC, BD, DM, ICOND, ROHM
COMMON/A2/DIF, DIF1, TKN, TKP, TIME, TK, TI1, E, H, TI2, M, TMB
COMMON/A3/TT, SIGI
RHOC=2.87E03*0.16*4.184E03
D2=(THIC**2*RHOC)/(TIME*TK)
K5=0
125  K5=K5+1
T1(1)=TI1(1)

```

```

T1(11)=TI1(11)
D4=1.6744/(H**2)
D5=D4/2.
105 K9=0
    K9=K9+1
    DO 85 K3=3,9
    TI=TI1(K3)
    IF(K9.GE.2)TT=(TI1(K3)+T1(K3))/2.
    ICOND=2
    CALL ROSE
    D6=D5*(TI1(K3-1)+TI1(K3+1))+(D2-D4)*TI1(K3)
    BN(K3)=D6+(THIC*E)**2*SIG1
    BN(K3)=BN(K3)/(D2+D4)
85 CONTINUE
    TI=TI1(2)
    IF(K9.GE.2)TT=(TI1(2)+T1(2))/2.
    CALL ROSE
    BN(2)=D4*TI1(1)+(D2-D4)*TI1(2)+D5*TI1(3)+(THIC*E)**2*SIG1
    BN(2)=BN(2)/(D2+D4)
    TI=TI1(10)
    IF(K9.GE.2)TT=(TI1(10)+T1(10))/2.
    CALL ROSE
    BN(10)=D5*TI1(9)+(D2-D4)*TI1(10)+D4*TI1(11)+(THIC*E)**2*SIG1
    BN(10)=BN(10)/(D2+D4)
    R1=D5/(D2+D4)
    IF(K9.GE.2)GO TO 205
    T1(2)=BN(2)
    DO 80 K2=3,10
    T1(K2)=BN(K2)+R1*T1(K2-1)
80 CONTINUE
    K8=0
205 K8=K8+1
    DO 95 K4=2,10
    IF(K4.GE.10)GO TO 800
    IF(K4.LE.2)GO TO 805
    T2(K4)=BN(K4)+R1*(T1(K4-1)+T1(K4+1))
    GO TO 95
805 T2(K4)=BN(K4)+R1*T1(K4+1)
    GO TO 95
800 T2(K4)=BN(K4)+R1*T1(K4-1)
95 CONTINUE
    T2(1)=T1(1)
    T2(11)=T1(11)
    DO 109 K4=2,10
    TCHE=ABS(T2(K4)-T1(K4))
    IF(TCHE.GT.0.1)GO TO 108
109 CONTINUE
    GO TO 119
108 DO 111 K4=1,11
    T1(K4)=T2(K4)
111 CONTINUE
    GO TO 105
119 DO 120 K4=1,11
    TI1(K4)=T2(K4)
120 CONTINUE
    IF(K5.LE.9)GO TO 125
    DIF=TI(M)-TMB
    DIF1=ABS(DIF)
    IF(DIF1.LE.1.0)GO TO 406
    IF(DIF.LT.0.)GO TO 400
    TKP=TIME
    GO TO 405
400 TKN=TIME
405 DO 12 I=1,11
    TI1(I)=TI2(I)
12 CONTINUE
    GO TO 407
406 DO 14 I=1,11

```

```
14      T12(I)=T2(I)
      CONTINUE
115     PRINT 115,(T2(K4),K4=1,11)
407     FORMAT(2X,11F10.2)
      RETURN
      END
C      *****
C      SUBROUTINE ROSE
C      COMPUTATION OF ELECTRICAL CONDUCTIVITY
      -----
      COMMON/A1/THIC,BD,DM,ICOND,ROHM
      COMMON/A3/TT,SIG1
      SIG=- (2.3*1.25*1000./TT)
      SIG1=(100./1.334)*EXP(SIG)
      IF(ICOND.EQ.1)GO TO 72
      SIG1=THIC/(BD/SIG1+DM/(1./ROHM))
72     RETURN
      END
```



## APPENDIX 3

COMPUTATION OF SWITCHING TIME FOR TWO PROXIMATE  
GRAINS TO JOIN IN MOLTEN CONDITION UNDER THE ACTION  
OF AN ELECTRIC FIELD

\*\*\*\*\*  
A=SEMI MAJOR AXIS,B=SEMI MINOR AXIS  
\*\*\*\*\*

```

-----
DIMENSION RAD(15),CK(15)
COMMON/A4/TIME,RAD,CK,KK,LL,SMAJ,SMIN,TKN,TKP,ADIF1,ADIF
TIME=1.E-9;N1=9;N2=7
RAD(1)=100.E-10
DO 15 KK=2,N1
RAD(KK)=RAD(KK-1)+50.E-10
15 CONTINUE
CK(1)=0.01
DO 20 LL=2,N2
CK(LL)=CK(LL-1)+0.01
20 CONTINUE
DO 30 KK=1,N1
PRINT 120,RAD(KK)
120 FORMAT(25X,'RADIUS IN METER',E15.8)
DO 40 LL=1,N2
PRINT 130,CK(LL)
130 FORMAT(20X,'SEP. TO DIA. RATIO=',F5.2)
GO TO 90
80 TIME=TIME*0.1
90 CONTINUE
CALL SWDYN
IF(SMIN.LT.0.)GO TO 80
IF(ADIF1.LT.0.1)GO TO 45
IF(ADIF.LT.0.0)GO TO 50
70 TIME=TIME-0.1*TIME
CALL SWDYN
IF(SMIN.LT.0.0)GO TO 80
IF(ADIF1.LT.0.1)GO TO 45
IF(ADIF.LT.0.0)GO TO 60
GO TO 70
50 TIME=TIME+0.1*TIME
CALL SWDYN
IF(SMIN.LT.0.0)GO TO 80
IF(ADIF1.LT.0.1)GO TO 45
IF(ADIF.GT.0.0)GO TO 60
GO TO 50
60 METHOD OF BISECTION
TIME=(TKN+TKP)/2.
CALL SWDYN
IF(ADIF1.LT.0.1)GO TO 45
GO TO 60
45 CONTINUE
PRINT 100,(TIME,SMAJ,SMIN)
100 FORMAT(5X,'SWITCHING TIME=',E15.8,5X,'A=',F6.2,5X,'B=',
1E15.8/2X,127(1H-))
40 CONTINUE
30 CONTINUE
STOP
END

```

\*\*\*\*\*

SUBROUTINE SWDYN  
SOLUTION OF DYNAMICS OF SWITCHING

```

-----
DIMENSION RAD(15),CK(15)
DIMENSION PHIBX(-1:15),PHIBXT(-1:15),PHIBY(-1:15),PHIBYT(-1:15)
DIMENSION VX(-1:15),UY(-1:15),VY(-1:15),XX(-1:15),ALX(-1:15)
DIMENSION PHII(-1:12,-1:12),PHIF(-1:12,-1:12),U(-1:12,-1:12)
DIMENSION UX(-1:15),ALY(-1:15),V(-1:12,-1:12)
COMMON/A1/CO1,CO2,PHII,A1,B1,FUN

```

```

COMMON/A3/I,J,PHIBYT,PHIBXT,N4,N6,DX,DY
COMMON/A2/A,H,AK,B,PHIF,SUM1,SUM2
COMMON/A4/TIME,RAD,CK,KK,LL,SMAJ,SMIN,TKN,TKP,ADIF1,ADIF
H=0.1;AK=0.1
EP=30.;EPO=0.885418E-11;DENS=10.E3
A=RAD(KK);B=RAD(KK);SUTEN=0.0544
P=1.+CK(LL)
C=4.*SUTEN/(EP*EPO*RAD(KK))
E=SQRT(C*(P-SQRT(P)))
S01=(1.+CK(LL))*RAD(KK)*1.E10
PHIBX(0)=0.;PHIBY(0)=0.
UX(0)=0.;VX(0)=0.;UY(0)=0.;VY(0)=0.;XX(0)=0.
DO 10 I=1,10
XX(I)=XX(I-1)+0.1
PHIBX(I)=PHIBX(I-1)
PHIBY(I)=PHIBY(I-1)
UX(I)=UX(I-1);VX(I)=VX(I-1)
UY(I)=UY(I-1);VY(I)=VY(I-1)
CONTINUE
L=0
300 L=L+1
RAD1=RAD(KK)*1.E08
A3=A*1.E08
B3=B*1.E08
ALX(0)=1.0
I=0;X=0.
S0=CK(LL)*2.*RAD1
S=S0-2.*(A3-RAD1)
E=E*(S0/S)
C1=(0.75*EP*EPO*E**2)/DENS
C2=SUTEN/DENS
30 C3=2.303*C1*ALOG10(3./(3.-X**2))
C4=(A3/B3)**2*(1.-X**2)
C5=(A3/B3)*(C4+1.+X**2)
C6=(C4+X**2)**1.5
C7=(C5/C6)*(1./B3)
C8=(C2*1.E08)*(C7-2./RAD1)
C9=.5*(UX(I)**2+VX(I)**2)
C10=C3-C8-C9
PHIBXT(I)=PHIBX(I)+0.1*TIME*C10
Y=SQRT(1.-XX(I)**2)
IF(1.E0.0)GO TO 35
DO 36 J=0,10
IF(Y.GT.XX(J))GO TO 36
II=J-1
GO TO 37
36 CONTINUE
37 ALX(I)=(Y-XX(II))/H
35 CONTINUE
I=I+1
X=X+0.1
IF(1.LE.10)GO TO 30
DO 20 I=0,10
DO 25 J=0,10
PHII(I,J)=PHIBXT(5)
25 CONTINUE
20 CONTINUE
ALY(0)=1.0
I=0;Y=0.
40 X=SQRT(1.-Y**2)
C3=2.303*C1*ALOG10(3./(3.-X**2))
C4=(A3/B3)**2*(1.-X**2)
C5=(A3/B3)*(C4+1.+X**2)
C6=(C4+X**2)**1.5
C7=(C5/C6)*(1./B3)
C8=(C2*1.E08)*(C7-2./RAD1)
C9=.5*(UY(I)**2+VY(I)**2)
C10=C3-C8-C9

```

```

PHIBYT(I)=PHIBY(I)+0.1*TIME*C10
IF(I.EQ.0)GO TO 46
DO 45 J=0,10
IF(X.GT.XX(J)) GO TO 45
II=J-1
GO TO 47
45 CONTINUE
47 ALY(I)=(X-XX(II))/AK
46 CONTINUE
I=I+1
Y=Y+0.1
IF(I.LE.10)GO TO 40
-----
EVALUATION OF LAPLACE EQUATION BY GAUSS ITERATION
-----
A1=((A/B)*H)**2
B1=AK**2
C01=(1./A1)/(2.*(1./A1+1./B1))
C02=(1./B1)/(2.*(1./A1+1./B1))
L1=0
140 N4=9;N6=4;K=0
L1=L1+1
DO 50 J=0,9
K=K+1
IF(K.GT.5)GO TO 55
DY=ALY(J);DX=1.
IF(J.EQ.N6)DX=ALX(N4)
DO 60 I=0,N4
CALL FUNEAV
PHIF(I,J)=FUN
60 CONTINUE
GO TO 50
55 N4=8;N6=5
IF(K.GT.6)GO TO 65
DY=ALY(J);DX=ALX(N4)
DO 70 I=0,N4
CALL FUNEAV
PHIF(I,J)=FUN
70 CONTINUE
GO TO 50
65 N4=7;N6=7
IF(K.GT.8)GO TO 75
DY=ALY(J);DX=1.0
IF(J.EQ.N6)DX=ALX(N4)
DO 80 I=0,N4
CALL FUNEAV
PHIF(I,J)=FUN
80 CONTINUE
GO TO 50
75 N4=5;N6=8
IF(K.GT.9)GO TO 92
DY=ALY(J);DX=ALX(N4)
DO 85 I=0,N4
CALL FUNEAV
PHIF(I,J)=FUN
85 CONTINUE
GO TO 50
92 N4=4;N6=9
DO 90 I=0,N4
DX=ALX(I);DY=1.
IF(I.EQ.N4)DY=ALY(N6)
CALL FUNEAV
PHIF(I,J)=FUN
90 CONTINUE
50 CONTINUE
DO 95 J=0,9
N4=4
IF(J.LE.4)N4=9;IF(J.EQ.5)N4=8;IF(J.EQ.6.OR.J.EQ.7)N4=7

```

```

IF(J.EQ.8)N4=5
DO 100 I=0,N4
DIF=(PHIF(I,J)-PHII(I,J))/PHII(I,J)
DIF=ABS(DIF)
IF(DIF.GT.0.01)GO TO 105
100 CONTINUE
95 CONTINUE
GO TO 130
105 CONTINUE
DO 110 J=0,9
N4=4
IF(J.LE.4)N4=9;IF(J.EQ.5)N4=8;IF(J.EQ.6.OR.J.EQ.7)N4=7
IF(J.EQ.8)N4=5
DO 120 I=0,N4
PHII(I,J)=PHIF(I,J)
120 CONTINUE
110 CONTINUE
GO TO 140
130 CONTINUE
DO 600 J=0,9
N4=4
IF(J.LE.4)N4=9;IF(J.EQ.5)N4=8;IF(J.EQ.6.OR.J.EQ.7)N4=7
IF(J.EQ.8)N4=5
DO 610 I=0,N4
PHII(I,J)=PHIF(I,J)
610 CONTINUE
GO TO 600
PRINT 620,(PHII(I,J),I=0,N4)
620 FORMAT(10E12.5)
600 CONTINUE
-----
COMPUTATION OF VELOCITY COMPONENTS
-----
N4=9;N6=4;K=0
DO 160 J=1,9
K=K+1
IF(K.GT.N6)GO TO 165
DY=ALY(J);DX=1.0
IF(J.EQ.N6)DX=ALX(N4)
DO 170 I=1,N4
CALL VELEAV
U(I,J)=SUM1
V(I,J)=SUM2
170 CONTINUE
GO TO 160
165 N4=8;N6=5
IF(K.GT.N6)GO TO 175
DY=ALY(J);DX=ALX(N4)
DO 180 I=1,N4
CALL VELEAV
U(I,J)=SUM1
V(I,J)=SUM2
180 CONTINUE
GO TO 160
175 N4=7;N6=7
IF(K.GT.N6)GO TO 185
DY=ALY(J);DX=1.0
IF(J.EQ.N6)DX=ALX(N4)
DO 190 I=1,N4
CALL VELEAV
U(I,J)=SUM1
V(I,J)=SUM2
190 CONTINUE
GO TO 160
185 N4=5;N6=8
IF(K.GT.N6)GO TO 195
DY=ALY(J);DX=ALX(N4)
DO 200 I=1,N4

```

```

CALL VELEAV
U(I,J)=SUM1
V(I,J)=SUM2
200 CONTINUE
GO TO 160
195 N4=4;N6=9
DO 210 I=1,N4
DX=ALX(I);DY=1.
IF(I.EQ.N4)DY=ALY(N6)
CALL VELEAV
U(I,J)=SUM1
V(I,J)=SUM2
210 CONTINUE
160 CONTINUE
DO 710 J=1,9
N4=4
GO TO 710
IF(J.LE.4)N4=9;IF(J.EQ.5)N4=8;IF(J.EQ.6.OR.J.EQ.7)N4=7
IF(J.EQ.8)N4=5
710 CONTINUE
C
C
C
=====
EXTRAPOLATE TO FIND U,V ON BOUNDARY
=====
A2=A*H
B2=B*AK
UY(0)=(PHIBYT(0)-PHIF(9,0))/A2;VY(0)=0.
VY(10)=(PHIBYT(10)-PHIF(0,9))/B2;UY(10)=0.
DO 220 J=1,9
IF(J.EQ.6.OR.J.EQ.8)GO TO 230
IF(J.GT.4)GO TO 400
DIS1=SQRT(1.-(FLOAT(J-1)*0.1)**2)-SQRT(1.-(FLOAT(J)*0.1)**2)
DIS2=(ALY(J-1)*H-DIS1)
IF(J.GT.0.0.AND.J.LE.4)N4=9
PHI=(DIS1/(ALY(J-1)*H))*PHIF(N4,J-1)+PHIBYT(J-1)*DIS2/(ALY(J-1)*H)
UY(J)=(PHIBYT(J)-PHIF(N4,J))/(A2*ALY(J))
VY(J)=(PHIBYT(J)-PHI)/B2
GO TO 220
230 CONTINUE
IF(J.EQ.6)GO TO 240
VY(J)=(PHIBYT(J)-PHIF(J-2,J-1))/B2
UY(J)=(PHIBYT(J)-PHIF(J-3,J))/A2
GO TO 220
240 VY(J)=(PHIBYT(J)-PHIF(J+2,J-1))/B2
UY(J)=(PHIBYT(J)-PHIF(J+1,J))/A2
GO TO 220
400 CONTINUE
IF(J.EQ.7)N4=7;IF(J.EQ.9)N4=4;IF(J.EQ.5)N4=8
DIS1=FLOAT(N4+1)*H-SQRT(1.-(FLOAT(J)*AK)**2)
DIS2=H-DIS1
PHI=(DIS1/H)*PHIF(N4,J-1)+(DIS2/H)*PHIF(N4+1,J-1)
UY(J)=(PHIBYT(J)-PHIF(N4,J))/A2
VY(J)=(PHIBYT(J)-PHI)/B2
220 CONTINUE
VX(0)=(PHIBXT(0)-PHIF(0,9))/B2;UX(0)=0.
UX(10)=(PHIBXT(10)-PHIF(9,0))/A2;VX(10)=0.
DO 250 I=1,9
IF(I.EQ.6.OR.I.EQ.8)GO TO 260
IF(I.GT.4)GO TO 430
DIS1=SQRT(1.-(FLOAT(I-1)*0.1)**2)-SQRT(1.-(FLOAT(I)*0.1)**2)
DIS2=ALX(I-1)*AK-DIS1
IF(I.GT.0.0.AND.I.LE.4)N4=9
PHI=(DIS1/(ALX(I-1)*AK))*PHIF(I-1,N4)+(DIS2/(ALX(I-1)*AK))*PHIBXT(I-1)
UX(I)=(PHIBXT(I)-PHI)/A2
VX(I)=(PHIBXT(I)-PHIF(I,N4))/(ALX(I)*B2)
GO TO 250
260 CONTINUE

```

```

IF(I.EQ.8)GO TO 270
UX(I)=(PHIBXT(I)-PHIF(I-1,I+2))/A2
VX(I)=(PHIBXT(I)-PHIF(I,I+1))/B2
GO TO 250
270 UX(I)=(PHIBXT(I)-PHIF(I-1,I-2))/A2
VX(I)=(PHIBXT(I)-PHIF(I,I-3))/B2
GO TO 250
430 CONTINUE
IF(I.EQ.7)N4=7;IF(I.EQ.9)N4=4;IF(I.EQ.5)N4=8
DIS1=FLOAT(N4+1)*AK-SORT(1,-(FLOAT(I)*H)**2)
DIS2=AK-DIS1
PHI=(DIS1/AK)*PHIF(I-1,N4)+(DIS2/AK)*PHIF(I-1,N4+1)
UX(I)=(PHIBXT(I)-PHI)/A2
VX(I)=(PHIBXT(I)-PHIF(I,N4))/B2
250 CONTINUE
-----
COMPUTATION OF NEW BOUNDARY
-----
BF=B+AK*TIME*VX(0)
A=RAD(KK)*(RAD(KK)/BF)**2
B=BF
DO 800 I=0,10
PHIBX(I)=PHIBXT(I)
PHIBY(I)=PHIBYT(I)
800 CONTINUE
SMAJ=A*1.E10;SMIN=B*1.E10
IF(B.LT.0.0)GO TO 350
IF(L.LT.10)GO TO 300
ADIF=SMAJ-S01
ADIF1=ABS(ADIF)
IF(ADIF1.LT.0.1)GO TO 350
IF(ADIF.LT.0.0)GO TO 900
TKP=TIME
GO TO 350
900 TKN=TIME
350 RETURN
END
*****

SUBROUTINE FUNEAV
EVALUATION OF PHI FUNCTIONS
-----
DIMENSION PHII(-1:12,-1:12),PHIBYT(-1:15),PHIBXT(-1:15)
COMMON/A1/CO1,CO2,PHI1,A1,B1,FUN
COMMON/A3/I,J,PHIBYT,PHIBXT,N4,N6,DX,DY
IF((J-1).LT.0)PHI1(I,J-1)=PHII(I,J+1)
IF((I-1).LT.0)PHI1(I-1,J)=PHII(I+1,J)
IF(J.EQ.9)GO TO 15
IF(I.EQ.N4)GO TO 15
FUN=CO1*(PHII(I-1,J)+PHII(I+1,J))+CO2*(PHII(I,J-1)+PHII(I,J+1))
GO TO 10
15 D=2.*(1./(A1*DY)+1./(B1*DX))
CX1=(2./(A1*(DY+1.)))/D
CA2=(2./(A1*DY*(DY+1.)))/D
CY1=(2./(B1*(DX+1.)))/D
CY2=(2./(B1*DX*(DX+1.)))/D
IF(J.EQ.9)GO TO 20
GO TO 30
20 PHII(I,J+1)=PHIBXT(I)
IF(I.EQ.N4)PHII(I+1,J)=PHIBYT(J)
GO TO 25
30 PHII(N4+1,J)=PHIBYT(J)
IF(J.EQ.N6)PHII(N4,J+1)=PHIBXT(N4)
25 FUN=CX1*PHII(I-1,J)+PHII(I+1,J)*CX2+PHII(I,J-1)*CY1+PHII(I,
1J+1)*CY2
10 RETURN

```

END

\*\*\*\*\*

SUBROUTINE VELEAV  
EVALUATION OF VELOCITY COMPONENTS U,V

```

-----
DIMENSION PHIF(-1:12,-1:12),PHIBYT(-1:15),PHIBXT(-1:15)
COMMON/A3/I,J,PHIBYT,PHIBXT,N4,N6,DX,DY
COMMON/A2/A,H,AK,B,PHIF,SUM1,SUM2
CF1=1./(2.*A*H)
CF2=1./(2.*AK*B)
IF(J.EQ.9)GO TO 15
IF(I.EQ.N4)GO TO 15
SUM1=CF1*(PHIF(I+1,J)-PHIF(I-1,J))
SUM2=CF2*(PHIF(I,J+1)-PHIF(I,J-1))
GO TO 10
15  CX1=1./(A*H*DY*(DY+1.))
    CX2=DY/(A*H*(DY+1.))
    CX3=(1.-DY)/(A*H*DY)
    CY1=1./(B*AK*DX*(DX+1.))
    CY2=DX/(B*AK*(DX+1.))
    CY3=(1.-DX)/(B*AK*DX)
    IF(J.EQ.9)GO TO 20
    GO TO 30
20  PHIF(I,J+1)=PHIBXT(I)
    IF(I.EQ.N4)PHIF(I+1,J)=PHIBYT(J)
    GO TO 25
30  PHIF(N4+1,J)=PHIBYT(J)
    IF(J.EQ.N6)PHIF(N4,J+1)=PHIBXT(N4)
25  SUM1=CX1*PHIF(I+1,J)-CX2*PHIF(I-1,J)-CX3*PHIF(I,J)
    SUM2=CY1*PHIF(I,J+1)-CY2*PHIF(I,J-1)-CY3*PHIF(I,J)
10  RETURN
    END

```



APPENDIX 4

```

CONSTRAINED OPTIMISATION PROGRAMME TO FIND THE OPTIMUM
COMBINATION OF FRACTIONS OF SPHERES, SINGLE STRAND CHAINS
AND F.C.C CLUSTERS USING SIMPLEX TECHNIQUE AND MG-PVS THEORY
*****
DEP(M,1)=DEPOLARISATION TRIPLET FOR SINGLE STRAND CHAIN
DEP(M,2)=DEPOLARISATION TRIPLET FOR F.C.C CLUSTER
ZI=X(1,1)=FRACTION OF SPHERE
SI X(1,2)=FRACTION OF SINGLE STRAND CHAIN
DPL(M)=DEPOLARISATION TRIPLET FOR SPHERE
EPMED=DIELECTRIC PERMITTIVITY OF GLASS MATRIX

```

```

-----
DIMENSION X(10,10),XH(10),XL(10),X0(10),XR(10),XE(10),XC(10)
DIMENSION F(10),Y(10,10),ABCOEF(100),DEP(5,5),EXALP(100)
DIMENSION XX(300),ALMD(100),EPB1(100),EPB2(100),ABCOE(100)
DIMENSION CSUM(10),CPEFUN(10)
COMMON N3,N4,XX,ALMD,EPB1,EPB2,DEP,EXALP,X,I,ALPHA,SUM1,PEFU
COMMON RK,ABCOE,ABCOEF,ICOND,WPB,TB,VFB,WPX,FIF,AVD,EPMED
N=2
N1=N+1
N2=N+2
WPB=(16.0*1.602E-12)/1.054E-27
TB=1.054E-27/(2.8381*1.602E-12)
VFB=1.822E08
WPX=WPB
FIF=.043
DATA A,B,C/1.0,0.5,2.0/
N4=13;N3=189
READ*,(ALMD(JJ),EPB1(JJ),EPB2(JJ),JJ=1,N4)
PRINT*,(ALMD(JJ),EPB1(JJ),EPB2(JJ),JJ=1,N4)
READ*,(XX(II),II=1,N3)
READ*,((DEP(M,M1),M=1,3),M1=1,2)
PRINT*,((DEP(M,M1),M=1,3),M1=1,2)
READ*,((Y(J,I),J=1,N),I=1,N1)
READ*,(EXALP(JJ),JJ=1,N4)
DO 550 JJ=1,N4
ZAPP=EPB1(JJ)
EPB1(JJ)=EPB1(JJ)**2-EPB2(JJ)**2
EPB2(JJ)=2.*EPB2(JJ)*ZAPP
CONTINUE
PRINT*,(XX(II),II=1,N3)
DO 5 I=1,N1
DO 6 J=1,N
X(I,J)=Y(J,I)
PRINT*,X(I,J)
CONTINUE
CONTINUE

```

# SIMPLEX OPTIMISATION TECHNIQUE

```

-----
K=0;ICOND=0
I=1;RK=.1
CALL FUNEAV
RK=0.3*SUM1/(-1.*PEFUN)
ICOND=ICOND+1
DO 15 I=1,N1
CALL FUNEAV
F(I)=ALPHA
CSUM(I)=SUM1
CPEFUN(I)=PEFUN
CONTINUE
K=K+1
K9=0
IH=1
K9=K9+1
FMAX=F(1)
DO 20 I=2,N1
IF(FMAX.GT.F(I))GO TO 20
FMAX=F(I)

```

```

      IH=1
20      CONTINUE
      DO 22 J=1,N
      XH(J)=X(IH,J)
22      CONTINUE
      FMIN=F(1)
      IL=1
      DO 25 I=2,N1
      IF(FMIN.LT.F(I))GO TO 25
      FMIN=F(I)
      IL=I
25      CONTINUE
      DO 26 J=1,N
26      XL(J)=X(IL,J)
      AN=N
      DO 30 J=1,N
      SUM=0.
      DO 40 I=1,N1
      IF(I.EQ.IH)GO TO 40
      SUM=SUM+X(I,J)
40      CONTINUE
      SUM=SUM/AN
      X0(J)=SUM
30      CONTINUE
      DO 35 J=1,N
35      X(N2,J)=X0(J)
      I=N2
      CALL FUNEAV
      FX0=ALPHA
      SUM0=SUM1
      DO 45 J=1,N
      XR(J)=(1.+A)*X0(J)-A*XH(J)
      X(N2,J)=XR(J)
45      CONTINUE
      I=N2
      CALL FUNEAV
      FXR=ALPHA
      IF(FXR.LT.FMIN)GO TO 50
      DO 60 I=1,N1
      IF(I.EQ.IH)GO TO 60
      IF(FXR.LE.F(I))GO TO 65
60      CONTINUE
      GO TO 85
50      CONTINUE
      DO 55 J=1,N
      XE(J)=C*XR(J)+(1.-C)*X0(J)
55      X(N2,J)=XE(J)
      I=N2
      CALL FUNEAV
      FXE=ALPHA
      IF(FXE.LT.FMIN)GO TO 70
65      CONTINUE
      DO 75 J=1,N
      XH(J)=XR(J)
75      X(IH,J)=XH(J)
      GO TO 80
70      CONTINUE
      DO 90 J=1,N
      XH(J)=XE(J)
90      X(IH,J)=XH(J)
80      CONTINUE
      DO 95 I=1,N1
      IF(I.EQ.IH)GO TO 410
      GO TO 95
410     CALL FUNEAV
      CSUM(I)=SUM1
      CPEFUN(I)=PEFUN
      F(I)=ALPHA

```

```

95      CONTINUE
145     SUM=0.
        DO 100 I=1,N1
100     SUM=SUM+(F(I)-FX0)**2
        CONV=SQRT(SUM/N1)
        IF(CONV.LT.0.01)GO TO 105
        DO 700 I=1,N1
        DO 800 J=1,N
        Y(I,I)=X(I,J)
800     CONTINUE
700     CONTINUE
        IF(K9.GT.150)GO TO 500
        GO TO 110
85      CONTINUE
        IF(FXR.GT.FMAX)GO TO 115
        DO 120 J=1,N
120     XR(J)=XR(J)
115     CONTINUE
        DO 125 J=1,N
        XC(J)=B*XR(J)+(1.-B)*X0(J)
125     X(N2,J)=XC(J)
        I=N2
        CALL FUNEAV
        FXC=ALPHA
        IF(FXC.GT.FMAX)GO TO 130
        DO 135 J=1,N
        XH(J)=XC(J)
135     X(IH,J)=XH(J)
        DO 140 I=1,N1
        IF(I.EQ.IH)GO TO 400
        GO TO 140
400     CALL FUNEAV
        CSUM(I)=SUM1
        CPEFUN(I)=PEFUN
        F(I)=ALPHA
140     CONTINUE
        GO TO 145
130     CONTINUE
        DO 150 I=1,N1
        DO 155 J=1,N
        X(I,J)=(X(I,J)+XL(J))/2.
155     CONTINUE
150     CONTINUE
        DO 750 I=1,N1
        CALL FUNEAV
        F(I)=ALPHA
        CSUM(I)=SUM1
        CPEFUN(I)=PEFUN
750     CONTINUE
        GO TO 145
105     CONTINUE
        IF(K.EQ.1)GO TO 180
        FUN2=SUM0
        GO TO 190
180     FUN1=SUM0
        RK=0.2*RK
        DO 430 I=1,N1
        F(I)=CSUM(I)-RK*CPEFUN(I)
430     CONTINUE
        GO TO 170
190     DEV=ABS((FUN2-FUN1)/FUN2)
        PRINT*,DEV,RK
        PRINT*,(X0(J),J=1,N)
        IF(DEV.LT.0.005)GO TO 200
        PRINT 900,(ALMD(JJ),ABCOEF(JJ),EXALP(JJ),ABCOE(JJ),JJ=1,N4)
900     FORMAT(2X,4(4X,F10.5))
        RK=RK*0.2
        PRINT 950

```

```

950  FORMAT(3X,127(1H-))
      FUN1=FUN2
      DO 440 I=1,N1
      F(I)=CSUM(I)-RK*CPEFUN(I)
440  CONTINUE
      GO TO 170
200  PRINT 600,FIF,AVD
600  FORMAT(25X,'FILL FACTOR=',F6.4,25X,'PARTICLE SIZE=',F6.1)
      PRINT*,(X0(J),J=1,N)
      PRINT 250,(ALMD(JJ),ABCOEF(JJ),EXALP(JJ),ABCOE(JJ),JJ=1,N4)
250  FORMAT(2X,4(4X,F10.5))
500  STOP
      END
C *****
C SUBROUTINE FUNEAV
C EVALUATION OF OPTICAL ABSORPTION COEFFICIENT BY MG-PVS THEO
-----
      DIMENSION XX(300),ALMD(100),EPB1(100),EPB2(100),X1(100)
      DIMENSION NF1(100),F1(100),W(100),EPS1(100),EPS2(100)
      DIMENSION PEPS1(100),PEPS2(100)
      DIMENSION DEP(5,5),DPL(5),ALPH1(5),ALPH2(5)
      DIMENSION EPME1(100),EPME2(100),ABCOE(100),ABCOEF(100)
      DIMENSION X(10,10),EXALP(100),A3(100)
      COMMON N3,N4,XX,ALMD,EPB1,EPB2,DEP,EXALP,X,I,ALPHA,SUM1,PEF
      COMMON RK,ABCOE,ABCOEF,ICOND,WPB,TB,VFB,WPX,FIF,AVD,EPMED
      ZI=X(1,1)
      SI=X(1,2)
      AKI=(1.-(ZI+SI))
      IF(ICOND.EQ.1)GO TO 80
      EPMED=10.0
      EPM1=EPMED;EPM2=0.
      DPL(1)=1./3.
      DO 5 M=2,3
5    DPL(M)=DPL(M-1)
      AVA=0.
      SUM=0.
      BMAX=XX(1)
      DO 10 II=2,N3
10   IF(XX(II).GT.BMAX)BMAX=XX(II)
      CONTINUE
      K=0
      A=30.
15   B=A+5.
      K=K+1
      NF=0
      DO 20 II=1,N3
      IF(XX(II).GT.A.AND.XX(II).LE.B)GO TO 30
      GO TO 20
30   NF=NF+1
20   CONTINUE
      X1(K)=(A+B)/2.*1.E-8
      NF1(K)=NF;ANF=NF
      F1(K)=NF1(K)
      AVA=AVA+FLOAT(NF1(K))*(A+B)/2.
      SUM=SUM+X1(K)**3*FLOAT(NF1(K))
      A=B
      IF(A.GT.BMAX)GO TO 35
      GO TO 15
35   AVA=(AVA/FLOAT(N3))*1.E-8
      AVD=AVA*1.E08
      DO 40 J=1,N4
      W(J)=(2.*(22./7.)*3.E10)/(ALMD(J)*1.E-4)
      G1=((AVA+2.*TB*VFB)/(TB*AVA))**2+W(J)**2
      H1=W(J)**2+1./TB**2
      Q1=G1-W(J)**2
      EPS1(J)=EPB1(J)+(WPB/H1)*WPB-(WPX/G1)*WPX
      EPS2(J)=EPB2(J)+(WPX/W(J))*(WPX*SQRT(Q1)/G1)-(WPB/(TB*W(J))
      1*(WPB/H1)

```

```

40      CONTINUE
80      CONTINUE
      DO 85 J=1,N4
      K1=0
      A1=0.
65      R1=0.
      K1=K1+1
      DO 45 L=1,K
      IF(K1.GE.2)GO TO 48
      G1=((X1(L)+2.*TB*VFB)/(TB*X1(L)))*2+W(J)**2
      Q1=G1-W(J)**2
      PEPS1(L)=EPB1(J)+(WPR/H1)*WPB-(WPX/G1)*WPX
      PEPS2(L)=EPB2(J)+(WPX/W(J))*(WPX*SORT(Q1)/G1)-(WPB/(TB*W(J)
      1+(WPB/H1)
      A3(L)=(X1(L)**3*F1(L))/SUM
48      ALP1=0.
      ALP2=0.
      AP=PEPS1(L)-EPM1
      BP=PEPS2(L)-EPM2
      DO 50 M=1,3
      CP=EPM1*(1.-DPL(M))+PEPS1(L)*DPL(M)
      DP=EPM2*(1.-DPL(M))+PEPS2(L)*DPL(M)
      A2=CP**2+DP**2
      ALP1=ALP1+(1./3.)*(AP*CP+BP*DP)/A2
      ALP2=ALP2+(1./3.)*(BP*CP-AP*DP)/A2
50      CONTINUE
      A1=A1+A3(L)*ALP1
      B1=B1+A3(L)*ALP2
45      CONTINUE
      AI=EPS1(J)-EPM1
      BI=EPS2(J)-EPM2
      DO 55 M1=1,2
      ALPH1(M1)=0.
      ALPH2(M1)=0.
      DO 60 M=1,3
      CI=EPM1*(1.-DEP(M,M1))+EPS1(J)*DEP(M,M1)
      DI=EPM2*(1.-DEP(M,M1))+EPS2(J)*DEP(M,M1)
      A4=CI**2+DI**2
      ALPH1(M1)=ALPH1(M1)+(1./3.)*(AI*CI+BI*DI)/A4
      ALPH2(M1)=ALPH2(M1)+(BI*CI-AI*DI)/A4
60      CONTINUE
55      CONTINUE
      R1=Z1*A1+SI*ALPH1(1)+AKI*ALPH1(2)
      R2=Z1*B1+SI*ALPH2(1)+AKI*ALPH2(2)
      A=1.+(2./3.)*F1F*R1
      B=(2./3.)*F1F*R2
      C=1.-(1./3.)*F1F*R1
      D=(1./3.)*F1F*R2
      EPME1(J)=EPMED*((A*C-B*D)/(C**2+D**2))
      EPME2(J)=EPMED*((B*C+A*D)/(C**2+D**2))
      DEV1=ABS(EPM1-EPME1(J))
      DEV2=ABS(EPM2-EPME2(J))
      IF(DEV1.LT.0.01.AND.DEV2.LT.0.01)GO TO 70
      EPM1=EPME1(J)
      EPM2=EPME2(J)
      GO TO 65
70      ABCOE(J)=(W(J)/3.E10)*(EPME2(J)/SQRT(EPME1(J)))*1.E-4
      ABCOEF(J)=ABCOE(J)
      ABCOE(J)=ALOG10(ABCOE(J))
      IF(EPME1(J).LT.0.)PRINT*,ALMD(J),EPME1(J)
85      CONTINUE
      SUM1=0.
      DO 75 J=1,N4
      SUM1=SUM1+(EXALP(J)-ABCOEF(J))**2
75      CONTINUE
C      *****
C      FORMULATION OF INTERNAL PENALTY FUNCTION -PEFUN
      PEFUN=-1./X(I,1)-1./X(I,2)+1./(X(I,1)+X(I,2)-1.)

```

ALPHA=SUM1-RK\*PEFUN  
RETURN  
END

Addendum to section 2.2.4, chapter 2.

In section 2.2.4, it is true that we did not explicitly discuss the justification of the boundary conditions. Only we have referred to T. Kaplan and D. Adler's paper [Ref. 97, page 197] where similar boundary condition has been used for chalcogenide glassy material sandwiched between two metallic electrodes. The justification of this boundary condition is based on the assumption that the metallic electrodes have much higher thermal conductivity compared to glassy material so that the metallic electrodes can be treated as infinite heat sinks which fix the end temperatures at the surfaces of the sample to the experimental temperature. It has been stated in the same reference that for molybdenum metal and a typical chalcogenide glass the ratio of thermal conductivity of metal to that of glass is approximately 500 and this fact makes the infinite heat sink assumption an excellent one. Our glass sample is also sandwiched between two metallic electrodes of noble metal gold. For gold [Ref. R. C. Weast, ed., CRC Handbook of Chemistry and Physics, 61st edition (CRC Press, Inc., Boca Raton, Florida, 1980-'81)] and soda-lime-silica glasses [Ref. W. D. Kingery, Introduction to Ceramics (Wiley, New York, 1967)] the ratio of thermal conductivity of metallic gold to soda-lime-silica glass is approximately 190. This, therefore, justifies the boundary condition in section 2.2.4.



electric field (E) produces same voltage drop  $\Delta V = Ew$  between neighbouring layers of neighbouring grains. Here  $w = s_0 + d$  is the average separation between layers and  $s_0$  and  $d$  are average interparticle separation and diameter of particles respectively. Moreover has been assumed that the layers are roughly perpendicular to the macroscopic field. Therefore, if  $t$  be the thickness,  $V$  be the applied voltage and  $n$  be the number of layers,

$$E = \frac{V}{t} = \frac{V}{n(s_0 + d)} = \frac{(V/n)}{s_0 + d} = \frac{\Delta V}{s_0 + d}$$

Therefore applied electric field is uniform throughout the matrix and is perpendicular to electrodes. This is one of the assumptions (assumption 1, page 25) based on which the formulation has been made. Further it should be stated that the computed electric field ( $E_m$ ) between the neighbouring metallic particles is assumed to be related to the bulk electric field ( $E_m^b$ ) calculated on the basis of thickness by the expression (2.39a), page 38. This assumption is justified because of the large value of  $\rho_{\text{glass}}/\rho_{\text{metal}}$  ratio [Ref. 47, page 194],  $\rho$  being the electrical resistivity.

Addendum to section 2.2.1, chapter 2.

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It is true that when a metallic body is placed in a previously uniform field between two plates of a large parallel plate capacitor, the field around the metallic particle is distorted. The surface remains at constant potential, the field is perpendicular to equipotential surface and the force is proportional to surface charge density. But the system which has been investigated is very complicated because of the fact that a large number of metallic particles is distributed in the glassy phase. Therefore, applying these electrostatic principles to an individual particle and then extending to the large number of particles present in the system under investigation will be an intractable problem to solve. We have therefore followed an alternative approximate approach which is accepted in literature. [Ref. B. Abeles, Sheng Ping, M. D. Coutts and Y. Arie, Adv. Phys. 24, 407 (1975) ]. It has been stated in literature by Abeles et al that when an electric field is applied to a granular metal ( metal-dielectric composite ) it is reasonable to assume that the equipotential surfaces are approximately perpendicular to the applied macroscopic field and every metallic particle lies on one of the equipotential surfaces. These surfaces divide the whole granular metal sample into a large number of layers so that each particle lying on one of the layers is approximately at the same potential. Significant potential drop occurs between neighbouring grains only when they are in different